Rubber as a Construction Material for Corrosion Protection

A Comprehensive Guide for Process Equipment Designers

V. C. Chandrasekaran

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Dedicated to Esther Shine Peter, Jessica Peter, Abigail Arun and Christa Victor, my granddaughters, and Arputha Mary my wife.

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Preface

It is a well-known fact that most of the properties of rubber are complex due to its great deformability, i.e., when a piece of rubber is stretched or compressed in one direction it is compressed or stretched in another direction respectively. Rubber in fact behaves like a solid in one direction and like a liquid in another two directions. Two samples of rubber of the same composition and vulcanized side by side may give different test results due to variations in the early treatment of the rubber such as mastication and mixing or milling.

During the past two or three centuries there were only a few chemical engineering professionals who had an elementary understanding of rubber's properties and its processing with respect to its use as a material of construction, the relevance of this knowledge to the constructional design of, and the application to, chemical process equipment for protection against corrosion, as well as the implications of its elasticity, elastic recovery, and permanent set in chemical plant design. As these professionals rose in their careers most of them have made substantial contributions to the more successful and effective use of rubber in the process industries with the main focus on corrosion protection.

The main challenges presented by the chemical engineers as well as the several national and worldwide seminars and discussion forums conducted by associations of chemical engineers on the corrosion protection of their plant and equipment with rubber as a material of construction, and its longevity, contributed effectively to the expansion of the use of rubber within the rubber and the rubber-using industries.

The author observes that the industrial scenario is changing on a continuous basis although the knowledge of the chemical plant engineer in the usage of rubber remains stagnant. Though this book can be viewed as a standard text reference book on this specialized area of anticorrosive and sacrificial nature of rubber as a material of construction for corrosion protection in chemical plants and equipment, its scope is certainly wider and provides basic descriptions of corrosion protected plant and equipment in various process industries, their design, and fabrication. Extensive and detailed case studies of the application of rubber in the chlor-alkali, mining, paper and pulp, fertilizer and other core chemical processing industries are also documented.

Though rubber technology is not exclusively included as a branch in the chemical engineering curriculum, this work, the author hopes, will be an often-used reference book by the chemical and mechanical engineering professionals when selecting a material of construction from amongst a variety of materials, or when engaged in equipment design. At the same time, the book provides important rubber literacy and will be stimulating and fruitful to their profession. To the best knowledge of the author, there is currently no work exclusively dealing with rubber as a construction material to protect against corrosion even though rubber is used widely in chemical process industries as a economically viable and dependable material of construction.

Of necessity, this book contains basic details of fabrication of process plant and equipment in various chemical industries. Repetition here and there is unavoidable as the sole objective of this guide is to make sure the reader has the knowledge immediately at hand.

The author would be delighted if this book becomes a sought after book for the chemical engineers, industries and corporations, students, and entrepreneurs. It is also hoped that students, engineers, technologists, and chemists of all levels of understanding and knowledge, will find in this book the precise information they seek about the corrosion resistance of rubber and rubber's uniqueness in serving as a material of construction for the process industry. It was assumed while preparing the book that the readers possess basic knowledge and understanding in physics, chemistry, and engineering.

The author wishes to underscore the point that rubber technology is a vast field of study, and no single rubber chemist or technologist has been able to write authoritatively, comprehensively, and critically on all aspects of this discipline starting, perhaps, from Harry Baron to Naunton through Davis and Blake, Whitby, Le Bras, and others. The knowledge in rubber technology is accumulating day by day through new innovations and discoveries in raw materials, process and application technologies. Most of the literature or books in rubber technology are compilations of different topics written by different authors. Therefore, it is unavoidable and inevitable that some topics are more up-to-date than others. Obviously, this book is not intended to be a full text on rubber technology but gives a body of information on this unique topic pertaining to rubber fields that cannot be found in many other books in the world of rubber literature.

The suppliers of rubbers and other raw materials have been releasing technical brochures and bulletins pertaining to the suitability of various rubbers and the rubber chemicals of various kinds and various application details based on their laboratory test data and field trials. These publications are extremely useful resources for understanding rubber technology and its diversified facets. For this reason the addresses of a few references of technical literature considered as valuable sources of information are given in the appendix.

Because of the competitive nature prevailing in the chemical process industries, I have been to a greater extent unsuccessful in collecting proprietary information from individual designers and manufacturers of chemical plant and equipment. For this reason some of the information may be either inadequate or may not be too detailed. I am happy, therefore, to welcome any constructive criticisms or suggestions for improvement in the present or distant future.

V.C. Chandrasekaran
Chennai, India
February 2010

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Introduction – Background and Reasons for Using Rubber as a Construction Material

1.1 Background

Prior to 1929, chemical process industries faced perplexing and growing problems. As more and more corrosive chemicals and compounds came into use, the need for a reliable and durable method of protecting mild steel and concrete storage tanks, process vessels, pickling lines, mixers, reactors, agitators, pipelines, tank trucks, railroad tank cars, ship tankers, and exhaust gas scrubbers against corrosion became imperative and the use of rubber as a construction material began to be recognized universally. The rubber industry, which was hitherto engaged in the technology development of consumer rubber products starting from erasers, raincoats, footwear play balls etc; to engineering products such as rubber tyres, and multifarious rubber components for all engineering applications, became alert to these problems of the chemical industry and introduced the first rubber lining in 1929 [1].

Since the advent of the first rubber lining, research and development work continued and today's rubber technology took a different shape from eraser-to-tyre technology to a more sophisticated high technology discipline known as anticorrosive rubber or acid resistant rubber technology, which is eminently and reliably depended upon by the process industries. Rubber as a material of construction was viewed with more seriousness than ever before by the chemical engineers and well recognized by the chlor-alkali, fertilizer and mining industries and the chemical processes in the oil well and nuclear industries. Today with higher temperature operations and with more complex and critical duty conditions such as nuclear radiation and high degree of thermal abuse as ablation in the rocket industry and mechanical abuse in ore mining industries, and other severe environmental conditions prevailing in the oil well industries, the rubber technologist is faced with challenges in the art of developing newer rubber compositions, compounding and processing technologies which are quite different from practices adopted for conventional products. The chief characteristics which make rubber of great importance to the mechanical or structural and chemical engineers are its strength, the adhesion and strength of its bonding to metals and other substrates, its all-round deformability which enables it to be used in extension, compression, shear, torsion or combinations of these, its resilience, its resistance to fatigue, its resistance to attack by corrosive chemicals, its resistance to abrasion, its good electrical properties, its wide latitude of properties by compounding and its ease of molding or forming to any shape and size. Rubber however has some limitations such as swelling in oils, ageing, ozone attack, and attack by flame, although most of them can be overcome to a great extent by compounding techniques and with the use of specialty synthetic rubbers. Acrylonitrile rubber can be used for oil resistance,, and the use of neoprene rubber and antioxidants in liberal doses greatly improves resistance to ageing and weathering, ozone attack and attack by flame.

Among the many reasons why rubbers are widely used in the process industries, three are considered as important. Firstly, rubber operates in a variety of environments and has usable ranges of deformity and durability and can be exploited through appropriate and more or less conventional equipment design principles. Secondly, rubber is an eminently suitable construction material for protection against corrosion in the chemical plant and equipment against various corrosive chemicals, acids and alkalies with minimum maintenance lower down time, negligible scale formation and a preferred choice for aggressive corroding and eroding environment. Thirdly, rubber can readily and rapidly, and at a relatively lower cost, be converted into usable products, having complicated shapes and dimensions.

Rubber is also used for protection of other materials against fire, heat and wearing. Rubber gives excellent performance as a construction material, in vibration and shock dampening, in elimination of structural noise and is the ultimate material for sealing systems. All basic properties are more or less present in all types of products. For each application individual functional properties are optimized to meet specific requirements.

Before going further into the various functional characteristics of rubber it is worthwhile to know the meanings of the terms "elastomer" and "polymer" which are synonymous with the term, "rubber" which means a material that when rubbed erases a pencil or pen mark. Michael L. Berins [2] describes the above terms in the following manner.

1.2 Elastomer

A material which at room temperature stretches under low stress to at least twice its length and snaps back to the original length upon release of the stress.

1.3 Polymer

A high molecular weight organic compound, natural or synthetic, whose structure can be represented by a repeated small unit, the monomer (e.g., polyethylene, isoprene and cellulose). Synthetic polymers are formed by the addition or condensation polymerization of monomers. If two or more different monomers are involved, a copolymer is obtained. Some polymers can be rubbers and some can be plastics. Plastics which are also high polymers can include both natural, or synthetic products but exclude rubber whether natural or synthetic. At some stage in its manufacture every plastic is capable of flowing under heat and pressure into the desired final shape.

1.4 Rubber

Any elastomer capable of rapid elastic recovery after being stretched to at least twice its length at room temperature from 0°F to 150°F at any humidity. Hevea or natural rubber can be considered as an elastomer.

Since the terms rubber, polymer and elastomer are synonyms, throughout this book these terms are used interchangeably.

Hishfeld and Pison [3] were quoted by W.J.S. Naunton as stating that rubber will never attain the position it deserves in the field of engineering until it has been investigated comprehensively and its behaviour can be calculated and measured in the same way as that of steel. However, the prediction of Hishfeld and Pison has not been proved to be true, since rubber is extensively used in mechanical, chemical and various other engineering fields including today in the nuclear industry, and it is used so, because it can do something which steel cannot do, namely combine softness and hardness in the same material due to its ease of deformation and more credibly can resist corrosion of acids and erosion of ores. It was not intended to be used as a construction material during the early times of its discovery, but at later stages it offered numerous possibilities with its specialty characteristics in developing various applications in the chemical process industries, and during the past several decades it has been an accepted and recognized material of construction world wide for many industries facing corrosion. Today rubber is indispensable.

1.5 Rubber Dampens

Rubber dampens by transforming kinetic energy into static energy. This basic rubber property is utilized in protection against explosion and impact and effectively reduces or eliminates noise, vibration and water hammer in pipelines and reaction tanks with agitators.

1.6 Rubber Seals

Rubber has very good sealing properties due to its pliable and elastic behaviour and is the best choice to make oil, water and gas tight seals in the most demanding environments in the chemical and other engineering industries.

1.7 Rubber Protects Corrosion Effects

Rubber is chemically resistant to most corrosive liquids, gases, salt water, ozone and UV light. These corrosive agents are commonly encountered in process industries, shipping and the offshore sector. Where steel is exposed to corrosion, it is protected with a rubber lining, or a total rubber or rubber inflatable structure itself is used. Rubber has very good wear resistant properties. It provides excellent protection for steel and other materials against abrasion and protects against solids and suspended particles.

1.8 Rubber Gives Thermal Insulation

To prevent clogging of subsea oil and gas piping by wax and hydrate formation it is necessary to insulate subsea equipment with material with very good thermal properties, low k-value (The k-value, or heat transfer coefficient, is the measured value of the heat flow which is transferred through an area of 1 m^2 at a temperature difference of 1 K - thermal conductivity; the time of rate of heat flow through unit area of a homogeneous material in a direction perpendicular to isothermal) [3] also known as lambda the thermal conductance; it is the physical property of a material expressing its ability to conduct heat [4], and high heat capacity. It is tough, impact resistant and has a very long service life.

1.9 Rubber Gives Passive Fire Protection

Certain types of synthetic rubbers such as neoprenes and hypalons when suitably compounded with asbestos fillers are flame resistant and give passive fire protection. This safety aspect is a key priority in many chemical and engineering industries as well. These fire protection technologies are used to protect structures and equipment against all types of fires including the extreme conditions of a jet fire.

1.10 Rubber is Ablative

Ablation means removal of material from the surface of an object by vaporization, chipping, or other erosive processes. The term occurs in Space Physics [5]. In space vehicle design, ablation is used to both cool and protect mechanical parts and/or payloads that would otherwise be damaged by extremely high temperatures. A low-density EPDM rubber is a fire stopping and fire proofing product that can be ablative in nature.

1.11 Rubber Wears

Rubber wear products for the mineral processing, fertilizer and materials handling industries, such as scrubber linings, rubber screening panels, wear resistant sheets, etc. are well recognized and eminently suitable materials of construction.

1.12 Rubber Bonds with Metal

Rubber bonds well with metallic surfaces with suitable adhesives and this property is well utilized in many applications in the chemical industry, such as lining, metal rubber bonded anti corrosive molded components, diaphragms etc.

1.13 Rubber is Impermeable

Rubbers like butyl, EPDM and neoprenes are unreactive to air and corrosive gases and are impermeable to them.

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5. website: www.deai.ie/glossary-of-BER-terms.html
6. http://en.wikipedia.org/wiki/Ablation

2

Rubber Compounding

2.1 Background

During the era of exploration in the botanical sciences, many people were seeking unknown plant species that could be useful to humanity. Of all the great achievements in the botanical discoveries, none was more impacting than that of the discovery of certain wonder trees which gave a substance of semi-liquid state which later was made as a substance called rubber. This was an unstable product and existed for a few centuries as a curious material. This tree was called by the explorers of the era as a "wonder tree" which received its botanical name as "Hevea Brasiliansis." This tree is the source of virtually all the world's natural rubber production. Cutting the bark of the tree releases a substance called latex which is then collected, preserved and stabilized. This process is called "tapping." The latex is located in the inner bark of the tree and flows in the capillary vessels of the tree. Latex in the tree acts as a defense against insects damaging the tree. Crude hevea rubber is prepared from latex by two methods, namely 1) coagulation and subsequent treatment of the coagulum which involves washing and drying in the case of pale crepe and drying and smoking in case of smoked sheets and

2) drying by evaporation. During these processes the rubber globules in the latex give up their separate existence and fuse into one homogeneous mass of crude rubber.

Way back in 1820, an Englishman by the name of Thomas Hancock was puzzled to see that this mass of rubber was tough and nervy. He was curious and during his study he cut this mass of rubber and found that the freshly cut surfaces were tacky and adhered to each other when joined. But the uncut surface was not. He concluded that fresh surfaces if made large enough could adhere together and become soft enough for working further to form a desired shape. This adhering property or tack in a given quantity of rubber can be enhanced with heat and pressure. From this observation he invented a machine that cut and tore the mass and shredded the same. This machine was made of a hollow wood of cylindrical shape with studded core inside it and rotated with the help of a handle. During rotating a mass of rubber with the studded core, this machine chewed (masticated) it and made it softer and workable. Thomas Hancock did not want to patent this machine for fear of disclosure. He further gave a deceptive name to this machine as "Pickle" so that none could understand what it was and for what purpose it was used. In the history of compounding of rubber, this machine, truly a masticator which was actually doing the work of mastication of rubber, one of the basic rubber processing operations, was known as "Hancock's Pickle". Hancock kept notes during the process of his invention. He made the following comments: "pieces with fresh cut edges would perfectly unite; but the outer surface, which had been exposed, would not unite... it occurred to me that if minced up very small the amount of fresh-cut surface would be greatly increased and by heat and pressure might possibly unite sufficiently for some purposes"[1].

D is the handle for opening/locking the lid C, and 'F' is the masticated rubber. A is the hollow cylinder. B is the clamp and E is the studded core.

In later stages, the technology developed and rubbers were compounded, mixed in mills, calendered in calenders, extruded in extruders, molded in hydraulic presses, cured in autoclaves and many hand operations of forming and curing became possible. State-of the art techniques of compounding were developed to produce rubber products of any shape and dimensions for many requirements.

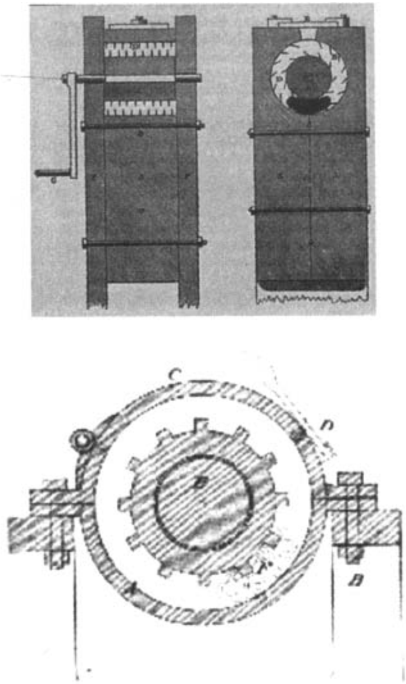

Figure 2.1 Hancock's Pickle.

Source: http://www.bouncing-balls.com/timeline/people/nr_hancock.htm

2.2 Compounding

Compounding of rubber is the development of rubber mixes which are required to effectively perform in service when made into finished products after vulcanization. At the same time the mixes should be capable of being processed in the factory without much difficulty and for minimum cost. Chemically speaking, a rubber compound is not a compound but is merely a mixture of rubber and compounding ingredients, ready for further processing in an extruder, calender, moulding press, vulcanizer or autoclave. Therefore compound in rubber parlance means mix. During vulcanization a chemical reaction takes place. The simplest of all compounds, namely rubber, and the vulcanizing agent is of little use in most engineering and industrial applications. However, it can be considered as a basic structure for making usable compounds. To make a usable product the base rubber must be admixed with various ingredients in addition to the vulcanizing agent. Uncompounded and unvulcanized rubber is not suitable for any use in most rubber products. The quality and durability and longer service life of rubber goods are possible only by the practical science of rubber compounding and vulcanizing. Raw uncompounded rubber has fewer applications which are based on properties such as swelling, solubility in solvents and tackiness which are aimed at being overcome in vulcanized goods. A certain amount of raw rubber is used for electrical tapes, and for manufacturing vulcanizing cements for patch works and for self-sealing surgical bandages. But this is only a negligible fraction of the total consumption of compounded vulcanized rubber.

2.3 Scope of Compounding

The scope of compounding includes specifying the type and amount of various ingredients in a mix, evolving the mixing procedure and vulcanization methods and their details accordingly. This basically covers the consideration of the requirements of the end use and the service properties of the products, processibility of the compounds and cost. The three most important factors to be considered in the development of a compound are:

- Choice of base rubber.
- The level of reinforcement with addition of fillers.
- The type of vulcanization system to be employed.

In general these factors determine cost, mechanical and visco-elastic properties, resistance to degrading environments and influences, processing characteristics of the compound, and special requirements such as flame resistance, oil resistance, low temperature flexibility, chemical resistance wear and abrasion resistance and non-toxicity requirements for application in contact with foodstuff, etc.

The manufacture of rubber goods consists basically of three steps.

- Compounding and mixing of rubber with proportionate amounts of various ingredients which when compounds are vulcanized yield the desired properties.

- Processing or the working of un-vulcanized compounded stock of rubber to form or build the articles to be vulcanized.
- The actual vulcanization.

In almost every compound formulation, all ingredients are listed in the general order that they are mixed into the rubber during the processing. The success of the whole process depends on the compatibility of the original mixed compound with each step in the further manufacturing operations. Therefore, the rubber compounder is responsible not only for the quality of the vulcanizates but also for the adaptation of these compounds to the manufacturing routine. There is a difference between laboratory scale compounding and factory scale compounding since the varying conditions in a factory environment are quite different from those in a laboratory.

Rubber compounding has undergone numerous changes during the last few centuries due to the advent of a variety of rubber chemicals and because of high demand from users of rubber products to meet their stringent duty conditions. During the past, it was a hit-or-miss affair in which it was usually necessary to make a large number of trial compounds before a suitable one was obtained. Now it is considered more as a science whereby a skilled compounder is able to predict with a fair degree of accuracy the general properties of any given compound formulation with a few trials only. A good knowledge of the properties of the rubber chemicals in general is therefore essential.

2.4 Basic Compounding Formulation

The basic compounding formulation specifies the minimum requirement of fillers, vulcanizing agents, and other substances that must be added to the rubber compound to achieve the desired properties. After the rubber, cure system and reinforcing filers have been selected it will be necessary to make several adjustments before all requirements are satisfied. It is generally sensible to start with the simplest mix formula for meeting the requirements. The recipe or the formula is usually written on the basis of hundred parts of rubber. For example if 5 parts of zinc oxide is to be added it is denoted as 5 phr (five parts per hundred rubber). Elementary compounding rules from the point of view of compound properties are discussed below.

2.5 Property Requirements of Un-vulcanized Rubber

2.5.1 Initial Compound Viscosity and Minimum Viscosity

This depends on the polymer type and increases with higher dry filler loading and reduces with peptizing agents, plasticizers, softeners, reclaimed rubber or resins.

2.5.2 Scorch Time at a Given Temperature

This generally depends on the type and amount of accelerator. The higher the accelerator the faster is the scorch. It can be made slow by the addition of retarders. Increasing softeners often slows down the onset of cure while at the same time improving internal lubrication in the compound. The higher the un-saturation in the rubber the faster is the scorch.

2.5.3 Optimum Cure Time

This has the same features as the scorch time in general. In compound design, choosing a curing system from this angle is very important since properties required are to be optimized.

2.5.4 Plateau Effect

The plateau time is the indication of sensitivity to overcure which is particularly relevant to thick articles. This varies widely with different classes of accelerators.

2.6 Property Requirements of Vulcanized Rubber

2.6.1 Stress-strain Properties

Tensile strength, modulus at a given elongation and elongation at break depend on the rubber type and the reinforcing filler type and its loading. NR by far gives the highest tensile strength when compared with synthetic rubbers, with the exception being polyurethanes. Finer type carbon blacks give higher tensile strength; high structure carbon blacks give higher modulus and better cure.

2.6.2 Hardness

This depends on total filler loading: the higher the loading, the higher the hardness. Softener loading reduces hardness.

2.6.3 Rebound Resilience

This property depends on filler particle size and filler loading. Higher filler loading gives lower resilience. Rubber type plays a great role here in that no synthetic rubber can match the characteristic of high resilience of natural rubber.

2.6.4 Tear Strength

It is similar to tensile strength from the compounding point of view. Fillers such as silica improve tear strength.

2.6.5 Permanent Set

This depends on the cross link density. With a tighter cure, permanent sets are low. Some high saturation polymers such as butyl rubbers have characteristically high permanent set.

2.6.6 Resistance to Abrasion

This is basically a polymer function and can be improved with loadings of reinforcing carbon blacks.

2.6.7 Resistance to Ageing by Heat, Oxygen and Metallic Contaminations

This property can be improved by the addition of antioxidants. Higher zinc oxide loadings increase resistance to heat ageing. Paraffin wax offers surface protection by blooming to the surface during curing. Low sulphur or sulphurless cure improves heat ageing considerably.

2.6.8 Resistance to Ageing by Ozone and Flexing

This property can be improved by the addition of antiozonants. Finer fillers give better flexing characteristics. Low sulphur or sulphurless cures, though good for heat ageing, are very bad for increasing flex life. Polysulphide links are preferred to mono or di-sulphide cross links.

2.6.9 Adhesion to Textiles

This depends on the viscosity (the softer the compound, the better is the adhesion) of the compound, sulphur (high sulphur gives good bonding), accelerator, zinc oxide (higher dosages of zinc oxide give better bondage), and stearic acid (up to a limit higher stearic acid gives better bonding) Certain thermosetting resins play a dramatic role in bond improvement.

2.6.10 Adhesion to Metals

This can be substantially improved by high black and high sulphur compounds. The only bottleneck is that not all metals are conducive to rubber bonding. Carbon steels are better than cast iron for bonding with rubber. Copper and zinc surfaces can be bonded with much ease.

2.6.11 Oil and Heat Resistance

These are based on polymer types. Neoprene, acrylonitrile, silicone rubbers and thiokol rubbers are to be chosen.

2.7 Basic Changes in Properties

As a rule-of-thumb based on shop floor experience, it can be noted that the hardness increases by 0.5 durometer with every increase of 1 phr of carbon black while addition of oil offsets this. Mineral processing oils produce a hardness drop of approximately 1 durometer for every two parts added. Optimum reinforcing carbon black loading generally falls in the region of 30 to 60 phr for most rubbers except silicones. Pure gum vulcanizates of high tensile strengths are possible with NR, IR, CR or butyl rubbers even without reinforcing fillers. Other rubbers such as SBR, NBR and BR have low gum strength inherently and require finer particle reinforcing fillers to develop maximum strength. Optimum abrasion resistance of compound is achieved by addition of around 50 phr of carbon black or silica filler. Modulus can be increased or decreased by adjusting the accelerator or sulphur levels. Compression set can be reduced by increasing crosslink density i.e., by adjusting sulphur /accelerator levels.

Functional properties such as swelling in oils and aqueous liquids and acid resistance, wear, fatigue life and corrosion protection, required for process industries are achieved by selection of suitable rubbers from among the various types of rubbers.

2.8 Compounding Ingredients

For a systematic consideration, the compounding ingredients can be conveniently classified in the following groups. However, the classification is somewhat arbitrary since some ingredients may be acting in more than one way. A brief outline of these chemicals is given with reference to compounding in the following paragraphs.

1. Raw rubber, reclaimed rubber.
2. Vulcanizing agents.
3. Accelerators of vulcanization.
4. Accelerator activators.
5. Accelerator retarders.
6. Antioxidants and ageing retarders.
7. Plasticizers and softeners.
8. Antisofteners or stiffeners.
9. Reinforcing fillers.
10. Inert fillers and diluents.
11. Pigments or colouring agents.
12. Factice or rubber substitutes.
13. Blowing agents for sponge rubber products.
14. Abrasives.

2.8.1 Raw Rubber

Raw rubber can be either natural or synthetic. The standard grades of natural rubber are smoked sheets and pale crepe. For high grade products, first grade smoked sheets, namely RMA IX or Pale Crepe, is used. Pale Crepe is practically colourless and is preferred in products where delicate colour, extreme whiteness or transparency is required. Smoked sheet is the rubber most commonly used in products subjected to wear and tear such as automotive tyre treads and carcasses, inner tubes, footwear, soles, cable covers, roll covers, tank lining and wire insulation. The lower grades of plantation rubbers are estate brown crepe or amber crepe. These are used alone or with smoked sheets either to lower costs or to increase the plasticity of friction and skim-coated compounds in the calendering machine or extruding machine. There are several synthetic rubbers available including general purpose ones such as styrene butadiene rubber and polybutadiene rubber as well as special purpose rubbers such as chloroprene, nitrile, butyl, EPDM and nitrile rubbers and many specialty synthetic rubbers. A detailed description of each, their types and properties is given in chapter 5.

Reclaimed rubbers were generally regarded as merely cheapeners or adulterants. However, in modern compounding practice it is not considered so. Its quality, uniformity and compounding properties have been so improved that it has now a definite place in rubber manufacturing. It has several processing advantages and it is liberally used in products where its presence is not specifically objected to. Reclaimed rubber aids in mastication of rubber, smooth calendering and extrusion and good mould flow. It is used extensively in mechanical goods, footwear, soles and heels, electrical goods, hard rubber products, rubberized fabrics etc. Its attractive advantage is its high rubber hydrocarbon content, as high as more than 50%. Reclaimed rubber, however, is kept out of certain products where high resistance to wear and tear rupture and ageing is desired. The general types of reclaimed rubber available in the market are given below:

Table 2.1 General types of reclaimed rubbers and their sulphur content

Source	Percentage of rubber hydrocarbon	Specific gravity	Percentage sulphur
Grey tube	60–65	1.12	3.25
Red tube	60	1.17	3
Whole tyre	50–55	1.16	2.75
Solid tyre	50–55	1.40	2.5
Footwear	30–35	1.58	5
Mixed stocks	30–45	1.25–1.45	2.5–4.5

The percentage sulphur (determined in the un-vulcanized reclaim) and the available rubber hydrocarbon are taken into consideration while evolving the compound formulation. It should be noted that reclaimed rubber is not all rubber. In arriving at the total rubber content in the rubber formulation containing reclaim, allowance must be made for its rubber content. For example in the following blend of smoked sheet and whole tyre reclaim, the total rubber content is to be considered as 100 parts instead of 125 parts as below and the proportion of other ingredients should be worked out accordingly on "parts per hundred rubber" (phr) basis.

Smoked sheet	- 75 parts
Whole tyre reclaim (rubber content-50%)	- 50 parts
Total	- 125 parts

The rubber content should be reckoned as 75 plus 25 (RHC of 50% of 50 parts of reclaim) = 100 phr.

2.8.2 Vulcanizing Agents

In the oldest but not a broader sense, vulcanization involved treating rubber at a suitable temperature with sulphur which was the earliest known vulcanizing agent. The discovery of various other agents known to produce vulcanizing effect, such as peroxides, nitro compounds, selenium or halogenated quinones has restricted the requirements of sulphur. Other methods such as physical vulcanization or the use of ultraviolet or cathode rays require neither heat nor sulphur. The introduction of sulphur monochloride process to effect vulcanization eliminated the requirement of elevated temperature. Addition of isocynate based cross linking agents speeds up vulcanization of rubber adhesives without addition of sulphur at ambient temperature. However sulphur still remains the principal vulcanizing agent and even ambient temperature vulcanization of rubber compounds by suitable compounding techniques has become possible with it.

Sulphur is a cheaper and the most practical ingredient available to effect vulcanization. In the early nineteenth century the practical dosage of sulphur for vulcanization was 6 to 10 parts per hundred parts of rubber. Due to the advent of accelerators it was reduced to about 0.5 to 4 phr. Later a sulphurless vulcanizing system was developed. Typical rubber-sulphur ratios for various products are given below.

Rubber lining	- 2.5 to 2.75 phr
Rubber roll covering	- 3 to 15 phr
Tyre carcass	- 2.5 to 3.5 phr.
Tyre tread	- 2.75 to 3.25 phr
Moulded tubes	- 0.75 to 2.5 phr
Footwear	- 2.00 to 2.50 phr
Soles and heels	- 3 to 4 phr
Mechanical goods	- 2.5 to 3.5 phr
Ebonites or hard rubber	- 20 to 40 phr

The reduction of rubber-sulphur ratio gives an advantage of bloom-free products in soft rubber goods. But this is an exception in the case of hard rubber or ebonite.

Auxiliary or secondary vulcanizing agents such as selenium or tellurium are sometimes used with low dosages of sulphur. Such low-sulphur compounds exhibit more or less stable tensile strengths at elevated temperatures. Hot vulcanization with ingredients other than sulphur has assumed commercial importance with the aid of thiuram disulphides which are sulphur bearing accelerators stable at atmospheric temperature. This type of sulphurless vulcanization is effected by using up to 5 phr of thiuram sulphides in place of sulphur. These ingredients are remarkable for the stability they impart to the vulcanizates which exhibit greater heat resistance and better ageing properties.

2.8.3 Accelerators of Vulcanization

Accelerators are second in importance only to sulphur. Their function is to accelerate the normally slow rubber-sulphur reaction, increase the rate of vulcanization, and increase productivity. Accelerators are classified into two main classes by types, namely organic and inorganic. The inorganic accelerators such as lime, litharge and other lead compounds and magnesia were employed extensively before the introduction of organic accelerators. They are still used mainly to produce hard rubber or ebonite products. Litharge is used in rubberized fabrics, insulated wires and cables and shoe compounds as well as chemical resistant rubber products for accelerating vulcanization. Organic accelerators can be considered as the backbone of rubber industry. Their use is practically universal. The main commercial types of organic accelerators are:

1. Benzothiazole derivatives
2. Thiuram disulphides
3. Salts of thio acids
4. Guanidine derivatives and
5. Aldehydeamines

The first three groups of accelerators are called ultra or semi ultra accelerators since they induce higher rates of vulcanization. The last two groups are called slow accelerators. These are effective at lower vulcanization temperatures, even as low as 110 to 120 degrees centigrade and with lower sulphur ratios, and generally bring about more lasting physical properties in the vulcanizates. The most important member of the first group (semi-ultra accelerator) is mercaptobenzothiazole which gives a pronounced flat curing effect or plateau effect i.e., prolonged vulcanization with little decrease in tensile strength and good ageing resistance. The second group is represented by tetra-methylthiuram mono, and disulphides and dipentamethylene thiuram tetra sulphide. These are called ultra accelerators and are used in much smaller dosages than thiazole derivatives. The thiuram disulphides are unique in that they accelerate and vulcanize rubber without addition of sulphur. Among the commercially important representatives of group 3, zinc dimethyl dithiocarbamate, zinc dibutyl dithio carbamate, piperidine pentamethylene dithiocarbamate and zinc butyl xanthate are all ultra accelerators effective at low temperatures and in small dosages.

In general and as a rule-of-thumb, accelerators of group 1 are used in proportions ranging from 0.5 to 1.5 parts per hundred rubber with sulphur dosages of from 2 to 3 phr. The more active accelerators of groups 2 and 3 should used in proportions from 0.25 to 0.5 phr in which case the sulphur dosage has to be 1.5 to 2 phr.

The commercially important representatives of group 4 are diphenyl guanidine and diortho tolyl guanidine. Group 5 includes a number of aldehyde aniline reaction products such as formaldehyde aniline, ethyledene aniline, butraldehyde aniline, heptaldehyde aniline hexa methylenetetraamine and acetaldehydeaniline. Aetaldehyde, butraldehyde and heptaldehyde derivatives of aromatic amines are powerful accelerators.

2.8.4 Accelerator Activators

Accelerators are usually unable to exercise their maximum effect unless the rubber compound contains certain ingredients known as activators of accelerators. These are of two kinds such as metallic oxides and organic acids. Both are very much and very often desirable activators for proper acceleration with most accelerators. Zinc oxide is the most commonly used metal oxide and added to nearly every compound in the proportion of at least 1 to 5 phr. Lead oxide (litharge) acts similarly but is less commonly used since it activates some accelerators so much that it tends to induce pre-vulcanization or scorching. Secondly, litharge darkens the vulcanizate and as such can be used only in black coloured products. Various grades of zinc oxides of different particle size and varying degrees of purity are available. Finer particle size zinc oxides are more active during vulcanization.

Organic acid activators are mono basic acids of high molecular weight such as stearic acid, oleic acid and lauric acids. These acids react with metallic oxides during vulcanization to form a rubber soluble salt or soap. This salt reacts with the accelerators enabling it to exert its full effect. Stearic acid is a more commonly used acid activator in compounds accelerated with benzothiazole compounds. Usually 1 to 2 phr dosage is sufficient. Oleic acid is generally avoided as it is detrimental to good ageing properties, unlike stearic acid. In compounds loaded with carbon blacks larger proportions of stearic acid is desirable when benzothiazole accelerator is used. A convenient rule to follow is to add 1 phr of stearic acid for every 10 parts of carbon black. In compounds containing considerable proportions of rosin or its blends as plasticizers, less fatty acid has to be used since the rosin acids themselves have activating properties. Certain vegetable oils such as palm oil contain sufficient amounts of fatty acids for activation. Many times the effects of one accelerator can be maximized by the addition of much smaller amounts of another accelerator, which is often called as "booster accelerator" or "secondary accelerator". For example the activity of mercaptobenzothiazole and its derivatives is greatly enhanced by small proportions of diphenyl guanidine or other basic accelerators and also by thiuram sulphides.

2.8.5 Accelerator Retarders

The rate of vulcanization of many of the industrial rubber compounds is very rapid. This is because of demands and constraints arising out of higher productivity, competition and cost consideration and employing high temperatures of curing. The faster a compound vulcanizes the more prone it is to premature vulcanization or scorching. Scorching is the onset of vulcanization at an undesirable stage of processing, making further processing impossible. The use of slow accelerators, which is dictated by the desire to vulcanize certain types of products at lower temperatures, aggravates the tendency to prevulcanize the compounds since the process temperature is high at about 90 degrees centigrade throughout the processing operations in mill, calender and extruder. No doubt better methods of mixing and processing, improved equipment designs and use of cooling devices have reduced this hazard in many modern factories. However, it has become essential to use certain ingredients which have a retarding effect on the rate of vulcanization at processing temperatures as a means of preventing scorching. Certain organic acids such as salicylic, phthalic, benzoic and even stearic acid in excess and phenols have retarding action. It is to be noted that salicylic acid accelerates vulcanization of neoprene compounds. However, the use of retarders is not very uncommon. Sometimes retarders produce porosity in vulcanizates. A good method of avoiding scorching in storage and during processing is proper choice of acceleratoring system, reduction of rubber-sulphur ratio, use of effective plasticizers, thorough cooling of the stock after mixing and subsequent processing and using the compounded stock within a reasonable time and proper storage temperature below room temperature say at around 20°C.

2.8.6 Antioxidants or Ageing Retarders

This class of rubber ingredients has sprung into existence because of the desire to reduce the deteriorating effects of the rubber products during storage and service life. This class comprises a number of organic materials without appreciable accelerating activity that retard deterioration and prolong the service life of the rubber products. They act largely as negative catalysts retarding oxidation reaction. The proportion of antioxidants usually added to a rubber compound varies from 0.5 phr to 2 phr. Certain of the antioxidants are used for protection against flex-cracking, increasing heat resistance and for reducing ozone cracks. Agents which protect rubber goods against ozone attack are called antiozonants. The antioxidants play no significant role in the vulcanization process. They serve to lengthen the life-span of vulcanized rubbers. The use of antioxidants or antiozonants in many cases in corrosion and wear applications is optional. But it has become customary to add these ingredients in most compounds, since the advantages of retardation of oxidation of rubber outweigh cost.

2.8.7 Plasticizers and Softeners

Mastication of rubber requires time and high power and consequently generates heat. It has therefore become necessary to accelerate mastication by adding certain ingredients which will soften and plasticize it so that it will reduce heat generation, power consumption and facilitate absorption of the various compounding ingredients. The softening is effected by the swelling of the rubber by the softeners. Mineral and vegetable oils, waxes, tars, resins etc; come under this class of ingredients. These organic ingredients are of different consistencies and softening action on the rubber. Their effectiveness varies greatly from one ingredient to another and the proportions in which they are added to rubber varies over a wide range. Some are used to aid plasticization and reduce the temperature of processing, others to impart tackiness or stickiness to the unvulcanized stock. Some of them act as lubricants reducing internal friction during filler addition and subsequent processing operations rather than actual plasticization of rubber. Stearic acid added for activation helps in plasticization and lubrication. Insufficient plasticization leads to non-homogeneous mixing and scorching and leads to nonuniform thickness and dimensions of sheets and profiles in the calendering machine as well as extruding machine with excessive shrinkage. On the other hand over plasticization makes the compounds too soft and sticky leading to difficulties in handling the same.

The fact that plasticization of rubber in the mixing mill is the result of oxidation implies that oxygen is indispensable for the same. Agents which accelerate oxidation thereby effecting plasticization to a desired mooney viscosity level are called peptizing agents.

2.8.8 Anti Softeners or Stiffeners

These are ingredients which when added in very small proportions to the compound stock produce a slight stiffening effect or decrease in plasticity. Benzidine and para amino phenol are examples of organic chemicals having this property. Litharge is an inorganic stiffener. These ingredients find use in compounds to reduce sagging or plastic flow during lining activity, wire insulation and hose compounds after calendering or extrusion and application and during vulcanization. Benzidine gives maximum effect in concentrations of about 0.1 phr.

2.8.9 Reinforcing Fillers

Compounds which contain only vulcanizing agents, accelerators and activators and no fillers are called "pure gum" compounds. Pure gum vulcanizates are not good enough for useful commercial applications. Products designed for most industrial applications must be compounded with relatively high proportions of certain ingredients which increase stiffness, hardness, strength of rubber and its resistance to abrasion, cutting and tearing. Such ingredients are called reinforcing fillers. Their effect in rubber is not chemical but physical depending mainly on the fineness and the homogeneous dispersion in rubber.

There is no clearcut demarcating line between fillers which reinforce and fillers which do not. Some may be considered as reinforcing in certain respects but not in others. But in general it can be classified that fillers which increase tensile strength, abrasion resistance, tear resistance or all three combined are called reinforcing fillers. These fillers which belong to the reinforcing class are various types of carbon blacks, zinc oxide, magnesium carbonate, silica and China clay. For maximum stiffening, tensile strength and abrasion and tear resistance highly reinforcing types of carbon blacks are used. For non-black vulcanizates zinc oxide and China clay are the reinforcing fillers. These fillers are also called for differentiating purpose as semi-reinforcing fillers. China clay causes high hardness and strength whereas resistance to abrasion and tearing are not greatly increased. Stearic acid coated calcium carbonates are superior to China clays particularly when high loading and resistance to tearing are required.

2.8.10 Inert Fillers and Diluents

These ingredients produce no noteworthy physical property improvements in rubber vulcanizates. They merely act as diluents and are chiefly used to increase volume, reduce cost and for manufacturing cheap consumable rubber sheets and other products where superior physical properties are not required. There are numerous types of fillers of this kind available such as whiting, barytes and ground minerals. Hard rubber dust is a common but important ingredient used in ebonite products for chemical resistant application and electrical components.

2.8.11 Pigments and Colours

Ingredients belonging to this class give colouring effect to rubber products. Zinc oxide and titanium dioxide produce light coloured articles and are used as a base for addition of other colouring ingredients. Organic dyes give bright and striking colours, and they can be used in smaller proportions than mineral pigments. Most of the dyestuffs used in textile industry can be used for manufacturing coloured rubber products.

2.8.12 Factice

Factices are products obtained by heating vegetable oils with sulphur (brown factice) or by treating them with sulphur chloride in a suitable solvent (white factice). They are called rubber substitutes. They have a mild softening action and are used in small proportions to aid extrusion and calendering operations. Factices are used in the manufacture of erasers and soft rollers. Brown factice in small proportion has a slight activating effect on vulcanization, while white factice has a retarding effect. Elastic bituminous substance derived from petroleum asphalt is known as mineral rubber which has a softening effect and as such is called a softener. Due to low cost and specific gravity asphalt is considered a cost reducing substitute. Its main disadvantage is that it can be used only in black coloured compounds. Hard asphalt has high dielectric strength and low dielectric constant and therefore it is used extensively in wire insulations.

2.8.13 Blowing Agents for Sponging

The manufacture of sponge rubber products such as gaskets for heat exchangers is based on the inclusion in the compound of chemicals which cause gas formation during vulcanization and thereby produce the desired porosity. Sodium bicarbonate and ammonium bicarbonate are examples of popular blowing agents.

2.8.14 Abrasives

These are special mineral ingredients employed to impart abrasive power to rubber products, used for abrading, grinding or polishing such as rubber erasers and hard or soft rubber grinding wheels such as carborundum.

Reference

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3

Ebonite-Problems and Solutions

3.1 Liquid Ebonite

There is a continuing need for protecting metals from corrosive chemical action, such as in metal pipes, stacks, chimneys, bridges, chemical plant constructions, ship hulls, and containers for aggressive chemicals, to name just a few applications. In addition to having a high resistance to chemical action, an ideal protective lining or coating has certain other properties: 1) the coating has the ability to be easily applied to the metal, e.g., by spraying, spreading, or free casting; 2) the coating has strong adhesion to many different metals; 3) it is strong, hard, abrasion resistant and thermostable; and 4) the hardening process of the coating can be performed in contact with moisture and does not require extreme or long heating, and does not release toxic fumes. An ideal metal coating may have many additional properties, depending on the particular application or purpose of the coating. The most widespread anticorrosive coatings possessing many of the above properties are polyurethanes and epoxide resins. The raw materials required to produce the coating are commercially available, inexpensive and non-hazardous.

These coatings have good chemical resistance to many substances, have adhesion to metals that is satisfactory for many purposes, and have good mechanical properties. However, neither polyurethanes nor epoxide resins satisfy all the criteria for an ideal coating for metal. In particular, although polyurethanes have outstanding oil-gasoline resistance, a unique combination of favorable physical-mechanical properties, and strong adhesion to some metals, they are not stable under elevated temperature, alkaline hydrolysis, and persistent tension. Epoxide resins, although they have outstanding adhesion to some metals, do not have a satisfactory resistance to acids, certain solvents, temperature changes, and vibration. One of the most significant problems associated with both epoxide resins and polyurethanes is their susceptibility to underfilm corrosion associated with defects in the coating surface. Because these coatings are bonded to the metal only by mechanical adhesive bonding, these bonds can be broken by the introduction of moisture, solvents or other substances.

There arose, therefore, a need for an anticorrosive coating for metals that overcomes the disadvantages in this prior technology. US Patent 5766687, issued on June 16, 1998 Estimated Patent Expiration Date, November 20, 2016, describes the development of a liquid ebonite coating for metals. The thickness of the applied layer of the liquid ebonite formulation is preferably in the range of approximately 0.1 mm to 0.3 mm. A layer less than 0.1 mm thick can still provide protection but is typically difficult to apply. A layer more than 0.3 mm thick will provide protection. To demonstrate the durability, metal sheets coated according to this new development were attached to a motor shaft and immersed in contaminated sea water. After two hours of rotation at 3000 rpm, conventional coatings of polyurethanes and epoxies demonstrate observable corrosion, while no trace of defects in the liquid ebonite coating was present [1].

However, for construction purposes, solid ebonites were chosen. As is known from rubber chemistry, solid ebonite, commonly known as hard rubber, is a polymer material with sulfur content used for vulcanization. Ebonite, like elastomeric or flexible rubber, is made from a combination of sulfur with polydienes (unsaturated rubbers containing double bonds). The sulfur and polydienes are combined with some auxiliary additives and heated to produce vulcanization. Typical mass ratios of sulfur to rubber are 2:100 for elastomeric rubber and 40:100 for hard rubber. Due to the large degree of sulfide cross linking formed in the vulcanization process, solid ebonite is a hard, non-flexible, plastic-like material possessed of unique chemical resistance to aggressive substances such as acids, alkalis, salt solutions, oil, and gasoline. In addition, solid ebonite has good mechanical properties. Consequently, these conventional rubbers are commonly used as materials for fuel tanks, containers for aggressive substances, and other applications.

Ebonite is an interesting material. It is a chemical resistant and electrical insulating material. It is machinable, and many engineering products can be made adopting regular engineering operations like turning, grinding, boring, drilling etc. However, it cannot be welded for making joints. It looks and is felt as a hard plastic. It is called hard rubber because it is a modified version of soft rubber but does not have the nature of soft rubber. Soft rubber has low percentage of sulfur and is elastic but hard rubber has lost most of its elastic or rubbery properties during conversion to hard stage. It is a highly vulcanized rubber and has low swelling in a given liquid media. Ebonite contains more than 30% sulphur combined with the natural rubber molecules. The commercial manufacture of hard rubber products started during the mid nineteenth century and henceforth ebonite became an important branch of the rubber industry. Though during the subsequent years and till today newer types of hard plastics came into existence to replace hard rubber, the hard rubber industry continued to stay in its position of importance by virtue of its unique characteristics, especially its chemical resistance. The chemical inertness, high strength and good appearance of ebonite and its machinability led to many applications with it in the process industries.

The ideal natural rubber ebonite was described long ago, as a compound with precisely one atom of sulphur per isoprene unit. And it was believed that such a compound actually existed and represented the upper limit of combination of sulphur with rubber [2]. However, the evidence for such an existence was later found to be not valid. Several postulations on the structure of ebonite were made by later research workers, and the final conclusion arrived at by them based on the behaviour of ebonite towards swelling liquids (aromatic hydrocarbons) was that ebonite formation during rubber-sulphur reaction during the vulcanization process led to a structure where the sulphur is attached to the tertiary carbon atom forming a ring structure. Further, it was concluded that there is no intermolecularly bound sulphur linking together adjacent isoprene chains of natural rubber molecules.

The elastic modulus of ebonite in its high elastic stage (i.e., at high temperature) is some ten times that of a pure gum soft vulcanized rubber, while its swelling in active swelling liquids is only about one-eighth and so the dependence of modulus and swelling on degree of cross linking indicate that ebonite is much more densely cross linked than a soft vulcanizate. Further it cannot be assumed that the quantitative relationships between cross linking, modulus and swelling in liquids deduced for natural rubber soft vulcanizates apply to the much more closely cross linked structure of ebonite.

The swelling time of ebonite is usually greater (10–15 times) than that for soft rubber in the same liquid. With soft rubber the swelling time is generally shorter. Soft rubber is resistant to the diffusion of ionic chemicals through the thickness. But ebonite has strong resistance to diffusion. As diffusion is inversely proportional to the thickness of the lining, the resistance to diffusion can be quadrupled by just doubling the thickness [3].

3.2 Rubber-sulphur Reaction

The hard rubber vulcanization reaction is generally a problematic one since it is exothermic, liberating considerable heat during the curing or vulcanization process. The overall heat produced in forming a natural rubber-sulphur ebonite is about 300 cal/gm of compound. Since the specific heat of the compound is 0.33, this heat would be theoretically sufficient to raise the temperature to about 1000°C. This problem is intensified in vulcanizing thick articles. This heat liberated suddenly at an early stage of vulcanization reaction is accompanied by a vigorous evolution of hydrogen sulphide gas, indicating that substitution or decomposition is taking place. Therefore, unless the greater part of this heat is dissipated during the vulcanization process, serious overheating will occur. At higher temperatures of vulcanization, sulphur combines chemically with rubber at a rapidly increasing rate. At 120°C to 130°C, the rate of reaction and consequent heat evolution is kept down. This, in conjunction with longer time available for heat flow from the centre of the mass of the compound results in only a moderate internal temperature rise compared with the result of vulcanizing at higher temperatures.

Hard rubber dust is used as a common filler in ebonite compounding to reduce this problem of explosive crack in ebonite vulcanization. It also facilitates mixing and reduces excessive shrinkage during processing. With the use of hard rubber dust the possibility of blowing or bursting during vulcanization is greatly reduced.

Vulcanization of thick articles of ebonite such as pipe internals for the chemical industry whose wall thickness is 1″ to 2″ poses this problem of heat evolution. Low temperatures and long periods of vulcanization were employed to alleviate this problem. Otherwise the material becomes porous and becomes a hard sponge and brittle mass as a result of excessive internal temperature. The general practice in the manufacture of thick articles is to use compounds containing high percentages of hard rubber dust, mineral fillers and reclaimed rubber which reduce the heat evolution during vulcanization. The use of accelerators should be done with caution in hard rubber vulcanization, especially of thick articles. Their use is at times attended with difficulties such as scorching, porosity, surface discolouration and brittleness in the final product. Further, the slow accelerators for soft natural rubbers will accelerate the hard rubber vulcanization fast. Example of this is diphenyl guanidine.

Another way to overcome the problem of exothermic reaction in ebonite vulcanization is to vulcanize the same in hot water for a long period, say for 48 hrs. Salt (sodium chloride) is mixed with the boiling water to elevate the boiling point to just above 100°C. This gives homogeneous and smooth vulcanizate free of any porosity. This procedure is adopted by some companies for vulcanizing a large number of pipe connectors of thickness as high as three inches built over metallic mandrels and the built in un-vulcanized connectors were hung in a large tank full of hot water which was heated by high pressure steam blown into the water which was agitated by an agitator for maintaining uniformity in curing temperature. Another method to control this exothermic reaction is to adopt a step-up curing process.

3.3 Retarding Accelerators

Accelerators might alter the distribution of heat evolution over the curing period and as such increase or decrease the temperature rise. The highest cure temperature (i.e., the critical curing temperature) that would just avoid a blow-out by preventing the exothermic temperature from rising is determined by experimental study. From the data the critical cure time required to reach the optimum properties when curing at the critical temperature is found to be the shortest in which optimum properties can be attained without excessive overheating. The critical curing time for different accelerators with 1.5 phr plus 5 phr of zinc oxide or magnesium oxide as well as without any accelerator which has the critical cure time as 100 is given below.

Table 3.1 Relative critical cure time for ebonite

Accelerators	**Relative critical cure time**
No Accelerators	100
Tetramethyl thiuram disulphide	75
Zinc Penta methylene dithiocarbamate	75
Zinc diethyl dithiocarbamate	65–80
Diphenyl guanidine	70
Butraldehyde aniline	60
Diphenyl guanidine plus magnesium oxide	53
Butraldehyde aniline plus magnesium oxide	40
Diphenyl guanidine plus zinc oxide	90
Butraldehyde aniline plus zinc oxide	85

In fact all the accelerators in this table above do shorten the critical time to some extent when compared with "no accelerator" level. Magnesium oxide added to either diphenyl guanidine or butraldehyde aniline shortens it still further; but zinc oxide has the opposite effect. This almost destroys the advantage gained by using the accelerator, thus retarding the reaction of vulcanization. It makes sense, therefore, to use less zinc oxide or no zinc oxide at all for autoclave curable ebonite compound formulations. However, addition of zinc oxide is ideal for compounds curable using a hot water curing method of vulcanization of large tanks lined with suitable low temperature curing compound formulation. There is an added advantage of fast conduction of heat due to the presence of a large quantity of zinc oxide in the compound. It becomes evident, therefore, that if an accelerator acted only during the non-exothermic stage (initial and final stages of the cure) it would make possible a shorter cure without the risk of overheating.

3.4 Coefficient of Vulcanization

The coefficient of vulcanization is usually defined as the number of units of weight of sulphur combined with 100 units by weight of unsaturated hydrocarbon. Ebonites prepared from natural rubber are

Table 3.2 Coefficient of vulcanization of natural and synthetic rubbers

Type of rubber	Theoretical coefficient of vulcanization at ebonite stage	Coefficient after correcting for rubber constituents
Butadiene rubber	59	59
Natural rubber/ polyisoprene	47	45
Styrene butadiene rubber	45	41
Butadiene acrylonitrile 75:25	44	43
Butadiene acrylonitrile 82:18	48	47
Butadiene acrylonitrile 65:35	48	47
Butadiene acrylonitrile 65:35	39	37
Butadiene acrylonitrile 60:40	36	34

vulcanizates that have vulcanization coefficients between 25 and 47. The theoretical coefficient value for natural ebonite is 47 while the values for the synthetic rubbers are more or less than this amount as shown in table 3.2. The theoretical coefficient values are all corrected for impurities present in the various raw rubbers.

3.5 Synthetic Rubbers Which Can Be Converted into Ebonite

Styrene butadiene rubber	Ebonite can be made
Polyisoprenerubber (Synthetic natural rubber)	Ebonite can be made
Butadiene acrylonitrile rubber	Ebonite can be made
Polybutadiene rubber	Ebonite can be made
Chlorobutadiene rubber	No successful ebonites are made from this rubber.
Polysulphide rubbers	Do not yield ebonite rubbers with high sulphur loadings.

Isoprene -isobutylene rubbers	Cannot be made into ebonite because of lack of unsaturation.

Butadiene acrylonitrile rubber (nitrile) can be compounded and cured to yield ebonites with interesting properties The amount of sulphur that combines chemically in nitrile rubber compounds corresponds to one sulphur atom per double bond. In this about 35 parts of sulphur per 100 of rubber and a curing time of 120 mts at 320°C are required. Coloured pigments can be incorporated in nitrile ebonite compounds. Organic diluents such as unsaturated petroleum products can be added to obtain tough semi ebonites. Nitrile rubber ebonites are used in steam valve disks, bonding abrasive grinding and cutting wheels.

Synthetic rubber ebonites do not fundamentally differ from natural rubber ebonites in swelling behaviour. Synthetic rubbers combine more nearly completely with the added sulphur. Nitrile ebonites are outstanding in that they are almost unaffected even by solvents such as benzene carbon-disulphide which strongly swell natural, butadiene and styrene butadiene ebonites [4,5].

3.6 Technological Aspects of Ebonites

Basic operations such as mastication, mixing, calendering and extrusion are similar for ebonite and soft rubber. The problems, especially in the compounding and vulcanization process which arise in the manufacture of ebonites, are quite different from those with soft rubbers and different tests are used for control of manufacture and for the assessment of the quality of the product. The outstanding differences between ebonites and soft rubbers are detailed below.

- Ebonite is chemically stable and so its resistance to ageing is remarkable and can be achieved without the use of antioxidants unlike soft rubbers.
- Reinforcement with carbon black or mineral ingredients is not possible. These reinforcing fillers affect the mechanical strength adversely and do not improve them. However the non-reinforcing fillers such as softer blacks and graphite and ebonite dust increase the resistance of ebonites to acids in an outstanding manner.

- Because of the dark colour of ebonites when vulcanized the possibilities of colouring is very limited and this is so with natural rubber ebonites.
- The vulcanization times for ebonites are very long when compared with those of soft rubber.
- There is a volume reduction of about 6% on vulcanization which necessitates a large allowance for shrinkage and special methods of curing like step-up cures.
- The chemical combination of rubber and sulphur is strongly exothermic when compared with soft rubber vulcanization. This is a very important factor for determining the method of vulcanization.
- Since all ebonite compounds contain high proportions of sulphur and usually large quantities of ebonite dust, the consistency of the compound during mixing and calendering prior to vulcanization is never that of a pure gum stock.
- In spite of a high proportion of sulphur used, blooming does not occur in fully cured ebonite vulcanizates.

3.7 Uses of Ebonites

It has been estimated that the consumption of rubber in ebonite products increased on an average of about 6% a year until 1951 when different plastics appeared in the market as competitive materials [6]. But because of the superiority of ebonites in acid and chlorine duties, it still maintains its place in the process industries as a material of construction as evidenced by its increased use in anticorrosive lining of chemical process vessels and tanks for the process industries and rolls for steel and textile and paper and pulp industries.

The choice between materials for a particular application may be determined by a combination of technical economic and aesthetic considerations. Ebonites have a great dimensional stability in moist conditions with freedom from deterioration caused by oxidation and excellent resistance to various chemicals. The temperature of use is limited where the material is under mechanical load, owing to its comparatively low softening point. This can be overcome by suitable compounding to some extent. A further weakness in appearance is the tendency of ebonite to develop an acid surface and to lose its deep black colour when exposed to bright sunlight, but this may not in any way affect its chemical resistance characteristics.

Natural rubber ebonites cannot be produced in brilliant colours which can be obtained with a number of synthetic rubbers like nitrile and resins such as high styrene. Ebonite products can be classified according to their primary uses as mentioned below.

3.7.1 Mechanical

Water meter components, pipe connectors, piston rings for hot water pumps, textile machinery accessories, and surgical apparatus.

3.7.2 Chemical

Chemical resistant pipes and tank lining, moulded anode rings for mercury cells, roller coverings and other chemical equipment linings.

3.7.3 Electrical

Sheets, rods, tubes and general mouldings.

Although there is a variety of ebonite formulations, most ebonites fall into one of the following types.

- Unloaded Ebonite: This is a high grade ebonite containing nothing but rubber and sulphur and high grade ebonite dust with no addition of any mineral fillers.
- Loaded Ebonite: In this class a mineral filler is added for green strength and to reduce deformation at higher temperatures.
- Flexible Ebonite: This can be called semi-ebonite usually loaded with mineral fillers with a lower proportion of sulphur, say 15 phr, and by incorporating into the compound synthetic rubbers like polychloroprene, polyisobutylene or butyl rubber. This ebonite will have good resistance to impact. A sheet made of flexible ebonite will look like a hard flexible leather.

3.8 Main Properties Exhibited by Ebonites

3.8.1 Yield at Elevated Temperatures

Whether used for mechanical or chemical engineering application, ebonite should not soften and yield under pressure at an unduly low temperature. The extent of deformation at a given elevated temperature is termed as yield, plastic yield or cold flow and the temperature at which a predetermined yield occurs under standard conditions of pressure and temperatures is referred to as yield temperature, plastic yield or softening point. At temperatures much above or much below the yield temperature, the material is obviously elastic.

3.8.2 Mechanical Strength

The second requirement in most applications is a definite degree of mechanical strength which is measured as tensile strength, cross-braking strength or crushing strength. The shape of the load-elongation curve for ebonite resembles that of metals in that after an initial stage of elastic extension it shows a fairly definite yield point after which much of the elongation takes place rapidly and irreversibly with little further application of load. This phenomenon is known as creep. A load elongation curve of this kind in the case of metals is shown below:

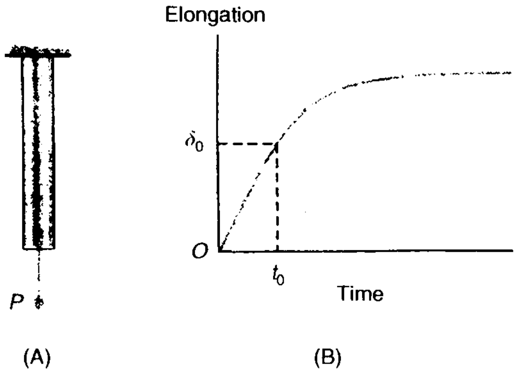

Figure 3.1 Load elongation curve FC.

In metals the above phenomenon manifests as shown in figure 3.1 [7]. For instance, when a vertical metallic bar is subjected to a load '*p*' for a given period of time "to" it produces an elongation equal to "δo" which is the yield point. Subsequent to the time "to" if the load is kept constant or without further application and the time duration increased, the bar gradually and slowly lengthens. Since this extension takes place only in a portion of the sample of ebonite under test, the tensile braking elongation is of little significance.

3.8.3 Impact Strength

The strength of a material when subjected to suddenly applied load is very different from that under steady or slowly applied loads and the former cannot be predicted from the knowledge of the latter. It is most significant in most cases of ebonite application to determine the energy of the smallest blow which will cause damage or rupture; especially when ebonite lined tanks and equipment and thin walled structures are handled, there is a likelihood of impact of the falling metallic objects such as hooks, bolts etc. on the surface of the ebonite. Thin walled ebonite lined structures deflect while handling. Proper handling technique is to be adopted in handling such structures to avoid any deflection and subsequent crack development on the surface of the ebonite lining. The blow which will crack the ebonite is much influenced by the presence of a notch or near the point of maximum stress due to deflection.

3.8.4 Volume and Surface Reactivity

A well compounded ebonite free from carbon black and hygroscopic ingredients and with its surface in a clean condition has a very high resistivity both through the mass of the material, and over its surface. It is so far above what is required for most practical purposes that it is seldom necessary to measure these properties, especially in cases of electroplating tanks lined with ebonite required in most steel plants.

3.8.5 Water Absorption

The diffusion of water into a mass of ebonite is so slow that the water absorbed affects only the material at the surface. In practice the degree of absorption would require many months or even years to complete on continuous exposure to water or dilute liquids.

3.8.6 Swelling in Organic Liquids

While considering swelling characteristics of ebonite two facts are noteworthy: 1) high sulphur and adequate cure reduce both the rate of swelling and the final amount of swelling, and 2) the synthetic ebonites are generally superior to natural rubber ebonites in resistance to swelling. Butadiene acrylonitrile, for example, is outstanding in this respect.

3.8.7 Acid Resistance

Hydrochloric acid forms a layer of rubber hydrochloride film when in contact with ebonite and this film prevents further reaction with the acid, thus protecting against corrosion. Similarly, wet chlorine forms a layer of chlorinated rubber film when in contact with ebonite, and this prevents further reaction with chlorine thereby giving protection against corrosion.

3.8.8 Density and Coefficient of Thermal Expansion

Density of ebonite is of no great practical significance . Coefficient of thermal expansion is a property which is sometimes of importance to design engineers. The volume coefficient of thermal expansion in an isotropic material like ebonite is three times the linear coefficient. An isotropic material is a material whose properties are not dependent on the direction along which they are measured.

3.8.9 Hardness

Within the range of fully vulcanized ebonite, hardness is not generally regarded as a property of great technical significance, but it is a necessary measure which is useful to control quality and to adhere to some routine product specification which is generally 80°D plus or minus 5°D in most chemical resistance lining applications. For flexible ebonites the hardness in general is 65°D plus or minus 5°D.

3.8.10 Machinability

Ebonite has good machinability and it can be easily subjected to machining operations such as turning, drilling, tapping, sawing, grinding and polishing with the least possibility of tool wear. In the industrial uses of ebonites such as in anticorrosive lining and roll covering, absence of chipping while drilling, grinding and other machining operations is of considerable importance. It is generally found in practice that an unloaded and fully cured ebonite is the best in this respect. Loaded ebonites as in the case of rolls for steel mills, textile mills and paper mills, surface grinding and polishing with suitable customised tooling devices become necessary. However, in practice difficulty is experienced if a proper tooling device is not adopted. The machining difficulty is experienced if proper tools are not employed. It increases with increased mineral content in loaded ebonites.

3.9 Processing of Ebonite

A substantial proportion of ebonites are produced in the basic form of sheets, rods and tubes from which the finished product can be completed by machining and polishing. The operations of mixing, calendering and extrusion call for no special and specific descriptions since they differ little from those applicable to soft rubber products. Sheets of up to 1/16 inches (1.5 mm) in thickness are produced directly by calendering. Thicker sheets are made by plying up layers of thin sheets. These sheets are rolled in spools with gada cloth liner backing and stacked in cool and dry storing conditions. If short sheets are to be cured in autoclave they are foiled with tin foils on both sides and each foiled sheet is separated by metal plates to assist in dissipating heat of reaction. A long slow rise and a long cure usually at a temperature of 140°C or less are necessary for uniformity. A step-up curing schedule in the autoclave for ebonite lined equipment is depicted in figure 3.2.

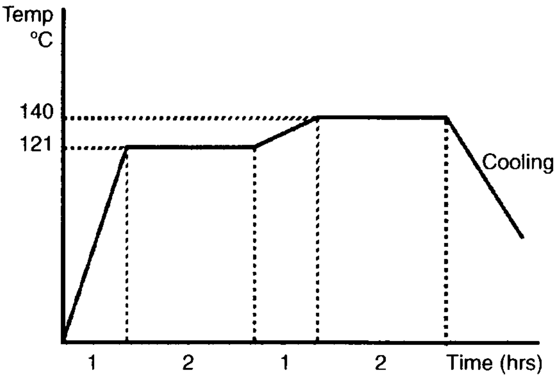

Figure 3.2 Step-up cure cycle for ebonite.

Thick walled tubes are built-up to the required thickness of say 25 to 50 mm from calendered sheets of about 1 mm thickness and the same is wrapped with wet cloth which gives additional pressure when shrunk, thus giving better consolidation. The tubes are built up on mandrels. The preferred method of curing is by using hot water.

3.10 Vulcanization in Relation to Properties

The ingredients in an ebonite compound influence the processing before vulcanization and the properties of the ebonite after vulcanization. These properties depend also on the degree and method of vulcanization. Even though vulcanization is the last major factory operation just before the finishing operation which may involve machining of the lining and ebonite covered rollers, it is better to consider the chemical and physical changes which take place during vulcanization of a simple rubber-sulphur ratio on the duration and method of cure. This leads to conclusions about the selection of optimum curing conditions.

3.11 Rubber-sulphur Ratio and Cure Time

If we take a rubber-sulphur ratio of 68:32 in an ebonite compound and then cure it at 155°C, the vulcanization coefficient increases practically to a constant value of 47 after about five hours and the uncombined sulphur decreases during the first four hours. This state may be called a full cure in the chemical sense. There is also a reduction in volume of about 6%. It is known that after the combination of the first few percent of sulphur, the material passes through a leathery stage with low strength and poor resistance to oxidation and with time passing a true ebonite is formed with increased impact strength.

If we increase the sulphur to a 65:35 ratio at full cure, the uncombined sulphur falls to about 4% while the vulcanization coefficient rises to about 49, but neither value is changed by further curing. At this stage tensile strength and cross braking strength are increased. Impact strength is reduced.

The effects of reducing the rubber-sulphur ratio from 68:32 to 72:28 are very significant. The uncombined sulphur can be reduced, the vulcanization coefficient being about 40. Tensile and cross braking strength are a little lower. Impact strength is much higher. An ebonite can be made with a still lower sulphur content but the outstanding physical and chemical resistant properties of a fully cured ebonite are sacrificed to a larger extent. For most purposes the useful range of rubber-sulphur ratio is from 68:32 to 72:28 and in practice a ratio of 70:30 is very commonly used as a compromise for several applications.

3.12 Curing Temperature

If the curing temperature is changed from one fixed already based on various considerations, the rate of combination of sulphur increases with temperature by a factor of about 2.3 per 10°C [8]. At the same time it appears that changes in physical properties depend on curing temperature in a way which cannot be accurately related to the chemical changes. This is most significantly seen in yield at elevated temperatures. With a 65:35 ratio cured at 155°C the yield temperature becomes almost a constant at a value of about 82°C after five hours. If the cure is carried out at 165°C, the yield temperature becomes constant for an equivalent period but at a value of about 2°C lower. At a lower cure temperature of 135°C, the yield continues to rise after combination of sulphur has ceased to a value of about 89°C after a time equivalent to ten hours at 155°C. Similar effects are found with a 70:30 ratio in the compound except that the continuous rise after full cure occurs at both 155°C and 135°C and not at 165°C. Although the gain in heat resistance by a long cure at 135°C is considerable, it is not considered as economic involving as it does a cure time of 50 hours. However the economic gain alone is not an appreciable advantage considering critical areas of applications in certain processing operations such as in electrolysis in mercury cells and reacting tanks in caustic soda industry where heat resistance is of paramount importance and this outweighs the cost involved in low temperature curing of ebonites. Furthermore, the high temperature resistance is achieved with hot water curing technique at a high temperature of about 110°C where the cure time involved is 48 hrs to 50 hrs. The boiling temperature of water is elevated to about 110°C by the addition of common salt (sodium chloride) in the water.

3.13 Method of Cure

Some of the technical properties of ebonite are appreciably affected by the method of cure. In open steam curing, the external pressure is limited to a few atmospheres of steam pressure. The direct exposure to steam during cure causes a yellowish discolouration which penetrates a short distance into the surface of the ebonite and may be objectionable unless the surface layer is to be subsequently removed. The steam also causes chemical changes in the outer layer of the ebonite due to hydrolysis of the non-hydrocarbon constituents of the rubber and there is a noticeable loss of sulphur by volatisation. Heat is easily transferred to the material in the early part of the cure and the temperature control by steam pressure is easy and precise.

In a hot water cure of sheets and thick articles like pipes and tubes, the disadvantage of direct contact with steam is avoided and heat transfer is more efficient than open steam in dissipating heat of the exothermic reaction. In natural rubber ebonites owing to the high proportion of sulphur and ebonite dust, the operation of mixing calendering and extrusion are very similar to those of highly loaded soft rubber mixing. Obviously the proportion of mineral fillers which can be absorbed is somewhat limited in ebonite compositions and additions of softeners such as paraffin wax and mineral oil are freely used as processing aids.

3.14 Shrinkage During Cure

Ebonite compounds shrinks to about 6% during cure and as such due allowance for a change of dimensions has to be made for this during manufacture. The ebonite dust and the mineral fillers added for controlling the exothermic reaction serves to reduce this shrinkage.

3.15 Shape Reduction During Cure

In open steam cure of linings and tubes and rods it is important that the ebonite does not flatten under self weight. Addition of ebonite dust and mineral fillers or reclaimed rubber increases the stiffness of the green stock and reduces the tendency for loss of shape.

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4

Rubber Lining – Types and Application Procedures

4.1 What is Rubber Lining?

Rubber lining is the skilled application of unvulcanized rubber sheets to prepared metal surfaces. The lined equipment is then vulcanized in a steam autoclave, fully bonding the rubber to the metal surface creating a durable and resilient protective rubber coating.

The rubber coating can be from 2 mm to 50 mm thick or more in certain cases depending on the application, and can be bonded to mild steel, stainless steel, cast iron and aluminium.

The principal benefits of rubber lining are its excellent resistance to corrosive and abrasive chemicals and materials, e.g., acids, alkalies, salt water, slurries, sand, shot blast media, crushed ores etc. In addition to this, rubber linings provide other benefits including noise and vibration reduction, electrical and thermal insulation and product protection.

Before proceeding with the discussion on rubber lining which gives corrosion protection to process equipment, it is appropriate to know some details about corrosion and general material selection along with rubber for combating the same. The following paragraphs cover the corrosion of materials and the selection of materials of construction along with recommended codes to be referred for practitioners in corrosion prevention.

Corrosion is the largest single cause of plant and equipment breakdown in the process industries. For most applications it is possible to select materials of construction that are completely resistant to attack by the process fluids, but the cost of such an approach is often prohibitive. In practice it is usual to select materials that corrode slowly at a known rate and to make an allowance for this in specifying the material thickness. However, a significant proportion of corrosion failures occur due to some form of localised corrosion, which results in failure in a much shorter time than would be expected from uniform wastage. Additionally, it is important to take into account that external atmospheric corrosion leads to many instances of loss of containment and tends to be a greater problem than internal corrosion. All these aspects of corrosive behaviour need to be addressed both at plant design time and during the life of the plant.

4.2 Types of Corrosion

Different forms of corrosion prevail in the chemical process industries as described in brief below.

4.2.1 Process Fluid Corrosion

Corrosion in metallic components occurs when pure metals and their alloys form stable compounds with the process fluid by chemical reaction or electrochemical processes resulting in surface wastage. Appreciable corrosion can be permitted for tanks and piping if anticipated and allowed for in design thickness, but essentially no corrosion can be permitted in fine mesh wire screens, orifice plates and other items in which small changes in dimensions are critical. Rates of corrosion can be heavily affected by temperature changes and whilst a material of construction may be suitable at one temperature, it may not be appropriate for use at a higher temperature with the same process fluid.

The corrosion of non-metallic materials is essentially a physiochemical process that manifests itself as swelling, cracking or softening of the material of construction. In many instances non-metallic materials will prove to be attractive from an economic and performance point of view. Rubbers especially are interesting materials of construction for the process industries by virtue of their unique properties which have a techno economic edge over other nonmetallic materials such as fibre glass reinforced plastics (FRP). It can be noted that where FRP is used it can be replaced by rubber, but where rubber is used it cannot be replaced by FRP, such as in applications in chlorine cells in caustic soda industries.

The use of various substances as additives to process streams to inhibit corrosion has found widespread use and is generally most economically attractive in recirculation systems, however, it has also been found to be attractive in some once-through systems such as those encountered in the petroleum industry. Typical inhibitors used to prevent corrosion of iron or steel in aqueous solutions are chromates, phosphates, and silicates. In acid solutions, organic sulphides and amides are effective.

4.2.2 Localised Corrosion

There are many forms of localised corrosion that can lead to early failure of equipment. The prevention of corrosion should be addressed at the mechanical design stage and proper design to minimise local corrosion should include free and complete drainage, minimising crevices, no dead spots in pipes and ease of cleaning and inspection. Pitting often occurs where certain impurities such as chlorides are present in process streams and cooling waters. This is an extreme form of localised corrosion. Once initiated, pits are usually self-accelerating and can result in rapid failures.

Many metals suffer from stress corrosion cracking under certain conditions. In piping the most frequent failures from stress corrosion cracking occur with stainless steels in contact with solutions containing chloride. Even trace quantities of chlorides can cause problems at temperatures above 60°C.

Crevice corrosion may occur where liquid is trapped between close fitting metal surfaces, or between a metal surface and a nonmetallic material such as a gasket. Attention to detail at the design and fabrication stage should be given to areas such as jointing to prevent crevice corrosion.

Localised erosion can occur where equipment orientation causes fluid velocities to accelerate such as at bends. Some chemicals can be handled in carbon steel piping, because they form protective coatings of ferric compounds in pipes. Careful design to ensure the coating is not eroded is necessary.

4.2.3 External Corrosion

Exterior surface corrosion or rusting of pipes occurs by the formation of iron oxides. Painting to an appropriate specification will significantly extend the period to the onset of corrosion, but the durability of the paint finish is largely dependent on the quality of the surface preparation as well as the thickness of the coated film. Improperly installed insulation can provide ideal conditions for corrosion and should be weatherproofed or otherwise protected from moisture and spills to avoid contact of the wet material on equipment surfaces. Application of an impervious coating such as bitumen to the exterior of the pipes is beneficial in some circumstances. Hypalon and neoprene rubber-based anticorrosive coatings admixed with chlorinated rubber are finding use in many installations.

Cathodic protection is an electrochemical method of corrosion control that has found widespread application in the protection of carbon steel underground structures such as pipelines and tanks from soil corrosion. The process equipment metal surface is made as the cathode in an electrolytic circuit to prevent metal wastage.

Anodic protection is less commonly used and relies on an external potential control system to maintain the metal in a passive condition. This form of corrosion protection has found practical application in the sulphuric acid manufacturing industry.

4.3 Materials Selection

Corrosion rates are expressed in terms of inches per year of surface wastage and are used to provide a corrosion allowance in the design thickness of equipment such as vessels and pipes. Operators will often use data based on historical experience from plant operations to aid them in determining appropriate corrosion allowances. Alternatively, corrosion charts are widely available that give corrosion rates for many combinations of materials of construction and process fluids, and normally a range of values will be provided for various process temperatures. In some instances, particularly where there is a mixture of chemicals present, appropriate data may not exist and corrosion tests may be necessary in order to determine the suitability of equipment. Operators should be able to demonstrate the use of corrosion allowances in equipment specification and design. The sources of data used should be traceable.

Whilst carbon and stainless steels are commonly used materials of construction, increasing use is being made of non-metallic and rubber lined equipment. The selection of the material of construction should take into account the cases of the worst process conditions that may occur under foreseeable conditions and should be applied to all components including valves, pipe fittings, instruments and gauges. Both composition (e.g., chlorides, moisture) and temperature deviations can have a significant direct effect on the rate of corrosion. The operator should demonstrate that procedures are in place to ensure that potential deviations in process conditions such as fluid temperature, pressure and composition are identified and assessed in relation to the selection of materials of construction for piping systems.

A wide range of rubbers are available for successful use as materials of construction and are applied in areas such as handling inorganic salt solutions where metals are unsuitable. The use of rubber linings is widespread in equipment such as tanks, pipes, and drums and most other critical chemical equipment. However, their use is limited to moderate temperatures, and they are generally suitable for use in abrasive duties. Some of the more commonly used plastics are PVC, PTFE and polypropylene.

The thin paint-like coatings are unlikely to give full protection due to defects, and the most dependable barrier linings are those that are built up in multiple layers to a minimum thickness of 3 mm.

4.4 Performance Tests

Normally, testing is carried out in order to determine the suitability of a material of construction for handling a process fluid. However, testing can be used for different purposes. Typically this might be to justify a modified inspection frequency of equipment on an existing plant.

There are a variety of test methods available. Commonly, test specimens consisting of small strips or standard samples of the material are exposed to the process fluid by immersion. The weight loss of the test specimen over a time period at the service temperature is measured in order to determine the corrosion rate. Testing can be carried out on the plant, in the laboratory, or on a pilot plant as demanded by situations.

Where laboratory testing is carried out using standard test methods, there are difficulties in interpreting results and translating them into plant performance. Care is required to ensure that the test fluid is exactly the same as on the process plant. Discrepancies in test conditions such as traces of impurities, dissolved gases, velocity, and turbulence can lead to erroneous results.

4.5 Maintenance Requirements

Process equipment handling hazardous materials should be inspected at regular frequencies, both internally and externally. Localised corrosion can be unpredictable and fabrication defects such as poor welds can be present. Linings can deform or be damaged. The frequency of inspection can be amended once an inspection history has been built up and the condition of a piece of equipment can be reasonably predicted. The operator should demonstrate that it has inspection and maintenance programmes in place for hazardous process equipment. Where equipment is lined, electrical continuity tests known as spark testing for lining defects such as pinholes should be carried out where appropriate. Cathodic and anodic protection systems should be regularly checked to ensure continued protection.

4.6 Control of Operating Conditions

Where control of corrosion is dependent on the concentration of contaminants or moisture, the operator should demonstrate that procedures and the necessary controls are in place to maintain a safe operating condition. Similarly, where inhibitors are added or systems such as cathodic protection are used, the operator should demonstrate that these systems are inspected and adequately maintained to ensure continued protection of the process.

4.7 Corrosive Chemicals

Brief details of the main corrosive chemicals which are handled in the process industry are given below.

4.7.1 Chlorine

The flow rate of liquid chlorine through carbon steel pipelines is restricted to 2 m/s to avoid removing the ferric chloride coating on the pipe surface which protects against erosion / corrosion of the carbon steel. Wet chlorine gas corrodes mild steel. Ebonite, or rubber lined steel is used for this duty. Chlorine gas handled at temperatures in excess of 200°C in carbon steel can result in chlorine / steel fires. Zinc can be used for this duty, but for low temperature (liquid) chlorine, special steels are required to avoid embrittlement. Titanium is unsuitable for chlorine duty and should be avoided. NR ebonites leave a strong pale creamy white chlorinated rubber deposit on the surface of the rubber, and this layer protects against further reaction of chlorine with rubber and as a result the equipment is free from attack.

4.7.2 Bromine

Susceptibility of materials of construction to attack by bromine is strongly dependent on the conditions of service including temperature, pressure and moisture content. Therefore, wherever possible materials selected for bromine duty should be tested under the actual conditions of use.

Storage vessels are commonly constructed of steel lined with lead, PVDF (and certain other fluoropolymers) or glass. If the bromine is "dry" then nickel or alloys such as Monel and Hastelloy can be used though all are susceptible to severe attack in the presence of wet bromine. Titanium is unsuitable for bromine duty (wet or dry) and should be avoided.

Lead is used for lining steel storage vessels and less frequently for lining pipes, but at high moisture contents and/or elevated temperatures the protective layer of lead bromide that forms on the surface of the metal is susceptible to degradation. Non-metallic linings including glass and certain fluorocarbon rubbers, including PVDF and PTFE have replaced lead in most applications.

Few metals are suitable for use in contact with "wet" bromine (moisture content in excess of 30 mg/kg). Niobium, tantalum and alloys of these two metals are suitable but high cost restricts their use (e.g., bursting discs and instrument components).

4.7.3 Sulphuric Acid

Corrosion protection of mild steel vessels occurs by the formation of an iron sulphate coating. Any condition leading to excessive turbulence can result in the removal of the coating and corrosion. Accelerated corrosion can also occur at air/acid interfaces due to interfacial dilution. Additionally, the temperature influence on corrosion rate varies with different strengths of acid and consequently it is necessary to define maximum operating temperatures. Chemical lead is sometimes used where steel is unsuitable and hypalon lining is found to be suitable in applications such as foot tanks or drying towers in caustic soda factories for drying of brine. Specially developed stainless steels have replaced traditional cast iron applications for high temperature duties.

4.7.4 Hydrochloric Acid

This acid is very corrosive towards most of the common metals and alloys. The corrosivity is increased where aeration or contamination by oxidising agents is present. Copper is particularly prone to this problem. Also many failures occur due to the presence of minor impurities such as ferric chloride. Rubber-lined steel is widely used for pipelines and large or small vessels. The rubber compound should be free from copper bearing antioxidants or accelerators.

4.7.5 Ammonia

Materials of construction for ammonia are dependent on the operating temperature. Whilst mild steel may be used at ambient temperature, special costly steels are required at low temperatures to avoid embrittlement. Impurities in liquid ammonia such as air or carbon dioxide can cause stress corrosion cracking of mild steel. Ammonia is highly corrosive towards copper and zinc. Rubber lined steel construction is suitable for service at ambient temperature.

4.7.6 Hydrofluoric Acid

Bulk storage of 70% acid or greater may be in mild steel semi ebonite lined (without silica filler). Polyethylene, polypropylene, and PVDF are commonly used for construction of other major components.

PTFE is often used for smaller components such as gaskets. Glass or GRP should never be used.

4.7.7 Oxygen

Materials suitable for liquid oxygen service are nickel steel, austenitic stainless steels, and copper or aluminium alloys. Carbon steels and plastics are brittle at low temperatures and should not be used on liquid oxygen duty. PTFE is the most widely used sealant.

4.7.8 Hydrogen

At temperatures below 120°C, carbon steel can be used up to high pressures. At elevated temperatures and significant pressures hydrogen will penetrate carbon steel and react with the carbon to form methane. This results in a loss of ductility and cracking or blistering of the steel. For high temperature applications steel alloys containing molybdenum and steel are satisfactory.

4.8 Codes of Practice Relating to Corrosion

The codes of practice relating to corrosion are given below as they are useful for practicing engineers

1. *HS(G)28 Safety advice for bulk chlorine installations*-Safety Advice for Bulk Chlorine Installations, HSE, 1999. www.hse.gov.uk
   Briefly deals with the limitations of some materials of construction for handling chlorine.
2. *HS(G)30 Storage of anhydrous ammonia under pressure in the UK : spherical and cylindrical vessels*, HSE, 1986 (Not in current HSE list).Gives advice for the appropriate materials of construction for ammonia storage vessels.
3. "Bromine in Bulk Quantities-Guidelines for safe storage and handling", Chemical Industries Association, 1989. Includes appendices containing guidance on materials of construction suitable for bromine duty.
4. ASME B31 (American Society of Mechanical Engineers - ASME) Guide for piping and piping systems A

Table 4.1 Industry applications and materials

Industry	**Applications**	**Materials**
Mining and Ore processing	Abrasion resistant linings for hoppers, chutes, cyclones, slurry pipelines, separators etc. Also bolt-in rubber wear plates for chutes and hoppers and conveyor rollers.	Soft natural rubber for abrasion resistance. Hardness range 40 to 70°A
Chemicals, Chlor alkali, Paper and pulp, Fertilizers, Oil drilling and Pharmaceuticals	Chemical resistant linings for storage tanks, road and ship tankers, process vessels, pipelines, valves, pumps, filters, agitators, centrifuges, impellers, etc.	Soft natural rubber or ebonite, neoprene, butyl and hypalon depending on operating temperature, and application.
Electroplating and Metal Finishing	Chemical resistant linings for cyclones, electroplating tanks, filters, pipelines and valves. Also wear resistant linings for vibratory finishing machines (barrels, bowls and tubs), shot blast chambers etc;	Ebonite, butyl rubber or EPDM linings for electroplating tanks. Soft natural rubber for vibratory finishing and shot blast machines.
Food and Brewing	Food quality linings for chutes, hoppers, process vessels, mixers, coating pans, pipelines etc.	White natural or neoprene food grade linings of 40 to 60°A.
Marine Industry	Corrosion resistant linings for fume scrubbers and cooling pipelines. Wear resistant linings for dredging pipelines.	Ebonite or hard rubber for corrosion resistance. Soft natural rubber for wear resistance.

Table 4.1 (cont.) Industry applications and materials

Industry	**Applications**	**Materials**
Materials Handling	Rubber lining for grabs, hooks and clamps. Wear resistant linings for chutes, hoppers storage bins etc. pulley rubber lagging for conveyor rollers.	Soft natural rubber for wear resistance. Various rubber materials for roller coverings.
Power Generation	Corrosion resistant linings for water treatment plant and cooling pipelines. Wear- resistant linings for coal handling plant, pulley rubber lagging for conveyor rollers etc.	Soft natural rubbers and other synthetic rubbers
Water and Effluent Treatment in Nuclear and other chemical plants.	Corrosion resistant linings for water treatment vessels and pipelines, pumps, valves, flowmeters, agitators, chemical dosing tanks, effluent tanks etc.	Soft natural rubber or ebonite, EPDM, butyl, neoprene or hypalon.
Civil Engineering	Wear and abrasion resistant linings for road rollers, compaction plates, and cement mixers.	Soft natural rubber.

comprehensive standard for the design of piping systems.

5. Choice of materials of construction for use in contact with chlorine, Euro Chlor. www.eurochlor.org A typical industry sector standard containing specific guidance on the use of materials of construction for chorine systems.
6. WRAS (Water Regulations Advisory Scheme that satisfy the Scheme's criteria based on British Standard

6920, the requirement for non-metallic materials in contact with drinking water in the UK).

4.9 Types of Rubber Lining

Different rubber materials for rubber linings are used for different areas of application such as lining for pipes, stirrer vessels, agitators, storage containers, road tank cars, railway tank cars and cargo ships, which are based on different base rubbers having unique attributes. Some of the critical rubber materials with their shop floor technical data and application areas are given below in brief for reference. These materials are to be properly formulated rubber compounds and based on vast and sound experience in designing with technical integrity.

4.9.1 Polychloroprene Lining

Polychloroprene material that may be vulcanized in the shop with hot air or steam in an autoclave or can self-vulcanize on-site within 2–3 months at ambient temperature of 25°C.

Specific weight	1.44 g/cm^3
Hardness	55 ± 5 Shore A
Abrasion resistance	max. 200 mm^3
Resilience	min. 25%
Maximum temperature	max. 85°C
Sheet length and width	10 m and width 1100 mm
Color	Black

The above material is expected to have excellent diffusion resistance to gases such as sulfur dioxide, nitrogen oxides and saturated water vapour and outstanding chemical resistance to mineral acids, bases, aqueous phases and polar solvents and weatherproof.

Area of application

Lining for Crystallisers;
    Flue gas desulfurisation plants;
    Pickling baths;

Pipes and fittings;
Storage tanks;
Road tank cars;
Railway tank cars;
Cargo ships.

4.9.2 Precured Bromobutyl Lining

Pre-cured bromobutyl material is a procured vulcanized bromobutyl rubber suitable for site lining and delivered with suitable adhesive system based on chlorobutyl, chloroprene and polyisocyanate.

Specific weight	1.27 g/cm^3
Hardness	50 ± 5 Shore A
Abrasion resistance	max. 320 mm^3
Resilience	min. 6%
Max. temperature	max. 85°C
Sheet length	10 m and width 1100 mm
Color	Black

Area of application

Lining for digesters in ore processing industry.

4.9.3 Autoclave Curable Bromobutyl Lining

Un-vulcanized bromobutyl material, to be vulcanized in an autoclave applied with a two-layer adhesive system.

Specific weight	1.27 g/cm^3
Hardness	50 ± 5 Shore A
Abrasion resistance	max. 320 mm^3
Resilience	min. 6%
Max. temperature	max. 100°C
Sheet length	10 m and width 1100 mm
Color	Black

4.9.4 Self Vulcanizing Bromobutyl Lining

Uncured bromobutyl material for self-vulcanizing construction site applications. Vulcanization requires about 3-4 months at an ambient temperature of 25°C.

Specific weight	1.27 g/cm^3
Hardness	50 ± 5 Shore A
Abrasion resistance	max. 320 mm^3
Resilience	min. 6%
Max. temperature	max. 100°C
Sheet length	10 m and width 1100 mm
Color	Black

Properties

Excellent diffusion resistance to gases such as sulfur dioxide, nitrogen oxides and saturated water vapour;

Weatherproof. Good chemical resistance to mineral acids, bases and aqueous liquors.

Area of application

Lining for Seawater desalination plants;
Pickling baths;
Stirrer vessels;
Filter vessels;
Slurry tanks;
Ion exchangers;
Pipe spools.

4.9.5 Self Vulcanizing Bromobutyl-Chloroprene Lining

Self-vulcanizing bromobutyl chloroprene material applied with the two-layer adhesive system with a subsequent thermal treatment. When the rubber sheet begins to vulcanize, bonding on steel is achieved using a suitable adhesive system.

Specific weight	1.3
Hardness	50 ± 5 Shore A
Abrasion resistance	max. 225 mm^3

Resilience	min. 10%
Max. temperature	max. 90°C
Sheet length	10 m and width 1100 mm
Color	Black

Properties

Good chemical resistance to mineral acids, bases and aqueous liquors. Outstanding resistance to media with oxidizing effects such as sodium hypochlorite and chromic acid.

Area of application

For corrosive chemicals, chloride and steel industry, especially for electroplating;

For storage and transport containers (lining of road and railway tank cars);

Lining of transport containers for transporting varying types of chemicals as well as mixed and used acids.

4.9.6 Autoclave/hot Water Curable CSM/PVC Lining

Un-vulcanized CSM/PVC material (chloro sulphonated polyethylene/polyvinyl chloride blend) for autoclave or hot-air vulcanization applied with the two-layer adhesive system.

Specific weight	1.20 g/cm^3
Hardness	73 ± 5 Shore A
Resilience	min. 20%
Max. temperature	max. 80°C
Sheet length	10 m and width 1100 mm
Color	Brown

4.9.7 Pre-vulcanized CSM/PVC Lining with Cold Bonding Adhesive System

Specific weight	1.20 g/cm^3
Hardness	65 ± 5 Shore A
Resilience	min. 20%
Max. temperature	max. 80°C
Sheet length	10 m and width 1100 mm
Color	Brown

Properties

Excellent diffusion resistance to gases such as sulfur dioxide, nitrogen oxides and saturated water vapour;
Good chemical resistance to mineral acids, bases and aqueous liquors.

Area of application

Lining for Seawater desalination plants;
Flue gas desulfurisation systems;
Stirrer vessels;
Filter vessels;
Slurry tanks.

4.9.8 Chlorobutyl-Chloroprene Rubber (CIIR/CR) Lining

Specific weight	1.24 g/cm^3
Hardness	55 ± 5 Shore A
Resilience	min. 8%
Max. temperature	max. 85°C
Sheet length	10 m and width 1100 mm
Color	Black

Properties

Outstanding resistance to chemicals with moderate concentrations and high solid contents;
Resists abrasion.

Area of application

Lining of plant components in ore dressing and fertilizer industries.

4.9.9 Autoclave Curable NR Lining

Un-vulcanized NR material that can be vulcanized in the workshop with pressurized steam (autoclave). Applied with the two-layer adhesive system.

Specific weight	1.13 g/cm³
Hardness	55 ± 5 Shore A
Abrasion resistance	up to 100³
Resilience	min. 63%
Sheet length	10 m and width 1100 mm
Color	Black

4.9.10 Pre-vulcanized NR Lining Bonded onto Steel with Cold Bond Adhesive System

Specific weight	1.13 g/cm³
Hardness	55 ± 5 Shore A
Abrasion resistance	up to 100³
Resilience	min. 63%
Sheet length	10 m and width 1100 mm
Color	Black

Properties

Good chemical resistance to mineral acids, bases and aqueous liquors. Outstanding resistance to media with oxidizing effects such as sodium hypochlorite and chromic acid.

Area of application

For corrosive chemicals, chloride and steel industry, especially for electroplating;
For acid pickling baths and electroplating baths.

4.9.11 Autoclave/hot Air Curable Butyl/PVC Lining

Un-vulcanized butyl rubber/PVC lining for autoclave vulcanization or hot-air vulcanization.

Specific weight	1.18 g/cm³
Hardness	62 ± 5 Shore A
Resilience	min. 12%
Max. temperature	up to 80°C
Sheet length	10 m and width 1100 mm
Color	Black

4.9.12 Pre-vulcanized Butyl Rubber/PVC Lining with Cold Bond Adhesive System

Specific weight	1.18 g/cm^3
Hardness	62 ± 5 Shore A
Resilience	min. 12%
Max. temperature	up to 80°C
Sheet length	10 m and width 1100 mm
Color	Black

Properties

Outstanding resistance to hydrochloric acid (HCl) up to maximum concentration;

Good chemical resistance to mineral acids, bases and aqueous liquors.

Area of application

Lining for Acid pickling baths and electroplating baths;

Tanks for manufacturing, storing and regeneration of hydrochloric acid.

4.9.13 Un-vulcanized Butyl Rubber/PVC Lining for Autoclave Vulcanization or Hot-air Vulcanization

Specific weight	1.18 g/cm^3
Hardness	62 ± 5 Shore A
Resilience	min. 12%
Max. temperature	up to 80°C
Sheet length	10 m and width 1100 mm
Color	Black

Properties

Outstanding resistance to hydrochloric acid (HCl) up to maximum concentration;

Good chemical resistance to mineral acids, bases and aqueous liquors.

Area of application

Lining for Acid pickling baths and electroplating baths;

Tanks for manufacturing, storing and regeneration of hydrochloric acid.

4.10 Application Procedures for Rubber Lining

Rubber lining is essentially a manual job. The lining is done on chemical process equipment using green rubber as well as pre-vulcanized rubber. A vessel lined with green rubber is vulcanized in an autoclave or by open steam or hot water. Vessels lined with pre-vulcanized rubbers are cured at ambient temperature. The lining sequence starts from the choice of compounds, equipment surface preparation, coating of adhesives and thereafter-actual lining of the rubber sheets onto the walls of the vessels. Stage-wise lining operations are described below.

The choice of compound depends on the duty conditions of the tanks / vessels to be lined. As an example, for all tanks in a phosphate based fertilizer plant, the lining can be natural, neoprene or butyl rubber based. These tanks sometimes handle phosphoric acids containing defoaming agents. When in the defoaming agent, oxo-alcohols are present, butyl lining can be used and if oleic acid is present, neoprene lining is suitable. When the de-foaming agents are minimal and the temperature is ambient and the tanks are used as mere storage vessels, natural rubber is used for lining. Similarly, for various equipment, handling different kinds of corrosive media and operating under a variety of conditions, careful scrutiny of the same is required.

Rubber lining of vacuum vessels is another critical task. Equipment such as vacuum evaporators and their accessories, vacuum de-chlorinator used in chlor-alkali plants, operate under high vacuum conditions. Rubber lining of such vessels calls for high quality material and workmanship. It is preferable that such vessels are vulcanized in an autoclave, wherever the size of the vessels suits the size of the autoclave. If the vessels cannot be accommodated in the autoclave because of size limitations, the lining is pressure cured using live steam, using the vessel itself as an autoclave with proper insulation outside. In such cases, the vessel should be designed to withstand the working pressure of at least 4-kg/cm sq gauges.

4.11 Role of Impurities

The presence of defoaming agents in phosphoric acid storage tanks would have to be known in advance by the rubber lining firm to enable them to take into account while compounding, as otherwise the rubber lining could fail. Depending on the type of rock phosphate, the addition of defoaming agents also varies. In many countries oleic acid is extensively used as a defoaming agent. While operating the plant from different sources of rock supplied, the amount of oleic acid added will vary widely and unless proper selection of the rubber material is made taking into account both the type and quantity of the defoaming agent present, damage to rubber lining could occur. Even though the original amount of oleic acid added in the storage tank may get progressively reduced in the downstream phosphoric acid along with sludge, etc., it is quite possible that there is accumulation of oleic acid around sharp corners. For example, in connecting bend pipes accumulation is possible in higher percentages up to 3% to 4% which cause damage to rubber lining. In anticipation of such an eventuality, it is preferable to line such equipment with neoprene rubber which is resistant to oleic acid. Similarly, in the case of handling and transporting hydrochloric acid, it is necessary to know the source of production of hydrochloric acid whether it is made by direct synthesis or obtained as a by-product from other organic industries. In the case of hydrochloric acid made by synthesis, there is no impurity which will affect the lining. In the manufacture of organic chlorinated products, the hydrochloric acid obtained as by-product contains a certain percentage of derivatives which attack the rubber lining. If the contamination is within the limit of solubility in hydrochloric acid, rubber lining may not get appreciably damaged. But if they go beyond the limit of solubility, the damage and swelling on the lining is very rapid. Generally, these chlorinated derivatives are heavier than hydrochloric acid, they get collected at the lower portions of the rubber lined tanks, and the lining gets damaged at these portions. Thus it is necessary that while specifying the medium handled, not only the main constituent is mentioned but also each impurity present is to be specified to enable the rubber technologist to choose a suitable lining compound. While operating the plant from different sources of rock supplied, the amount of oleic acid added will vary widely and unless proper choice of the rubber compound is made taking into account both the type and quantity of the defoaming agent present, damage to rubber lining could occur.

4.12 Working Temperature

Working temperature of the rubber lined vessels influences not only the proper choice of polymer but also the type of adhesive used for bonding. For temperature higher than the range of 70°C to 125°C, usually brick lining over rubber lining is provided to protect the rubber lining, thereby increasing the life of rubber lining.

4.13 Lining Thickness

The thickness of lining depends on the severity of corrosion or erosion. The diffusion of liquids is inversely proportional to the square of the thickness of the lining at a given temperature. That is to say, a 6 mm thickness is four times more resistant than a lining of 3 mm thickness. The speed of diffusion in the temperature range 30–80 deg C is proportional to the temperature increase. The fabricators of vessels are to be informed in advance that the vessel is meant for lining and should be asked to follow the standard procedure for fabrication of equipment meant for rubber lining.

To obtain a good lining, it is necessary that the lining surface either of mid steel, cast iron, stainless steel, aluminium, concrete, wood etc. should be fabricated/constructed avoiding sharp corners or edges. Sharp corners should be ground to have radius and the weld seams have to be ground flush. There must be accessibility by hand to all the surfaces to be lined. These criteria need not be applied to the lining of long pipes. In the case of long pipes, soft rubber bung of hardness 35°A/45°A is used as a tool for lining. However, spiral welded pipes lead to poor quality lining since the travel of the bung through the same will not be uniform and total air elimination cannot be guaranteed.

The welds should not be porous or should not have any cracks. As the lining is usually subjected to vulcanization in autoclave at a temperature of 130 to 150 deg C, the entrapped air inside the weld could expand and blow out the lining, necessitating repair work on the lined vessel.

After rubber lining, no welding or earthing should be done on the lined tank, so the lugs, hooks, pipe supports, etc. which may be required to be welded on the vessel, piping, etc. should be planned and completed at the time of fabrication of the vessel itself. The fabricator is normally informed about this in advance. In the case of concrete tanks, the concrete should be bone-dry through the entire thickness, and the lining surface should be free of dust, cracks, holes, etc.

For a perfect bonding between lining surface and adhesive, the surface must be absolutely cleaned free of oil, grease and contaminants such as, rust, chemical deposits, etc. In order to eliminate the rust and the scales from old steel vessels meant for relining, sand blasting is carried out twice. This will also provide the required roughness to the surface to be lined.

4.14 Adhesive Coating

Adhesives, prepared in the sigma-mixture, are tested for their viscosity and homogeneity, before applying to the surface of the vessel to be lined. It is usual to give a first and primer coat of the adhesive over the blasted surface immediately after sand blasting. Generally for lining and other interconnected operations, the humidity should not be very high. The preferred humidity is 60–70%. To enhance good adhesion, several primer coats are used on the metal surface. After coating, it is dried before the actual lining process, i.e, the application of calendered sheet. It is necessary to ensure that the solvent in the adhesive has completely evaporated as otherwise, during lining the volatile solvent will "blister" out and make the bonding poor.

4.15 Application of Calendered Sheet

The application of the calendered sheet onto the coated surface is the actual lining. The sheets should be laid on the coated surface without stretching. The air between the rubber sheet and the metal must be rolled out. The rolling is done with different kinds of rolls starting from 4" dia and up to 1-1/2" dia with face length of 2" with knurled surface or plain surface as might be required. The choice of the rolls depends on the place and the accessibility, like corners, acute angles, bends, etc. Taper cutting of the jointing edges, done manually, is a highly skilled job, requiring considerable experience. Very sharp edged knives and blades are used for cutting the sheets as per required profiles and sizes. The taper length should be four times that of the thickness and should be at an angle of 45°.

Lining sequence for each kind of vessel and piping should be planned ahead and the development of sheet to match the contours and shapes of the vessels is to be done meticulously, to achieve a perfectly finished and smooth lining. After the vessel is lined, it is ready for vulcanization either in the autoclave, or by open steam, or by hot water curing process.

As a principle, a responsible rubber lining manufacturer or applicator should be able to carry out the lining at any place and at any time. It will only be a question of additional auxiliary equipment and materials which might be required at times of different climatic condition. The main base metal surface is mild steel in the form of welded construction. Natural rubber lining is even today of great importance in acid-resistant applications. Ebonite lining, if subjected to low temperatures, tends to crack, which is obviously due to the thermal deformations in the tank. The danger of crack developments is due to the differing expansion coefficient of steel and ebonite and the handling of thin walled lined structures, i.e., they hit solid beams or other structural elements during handling. In order to combat such situations which are unavoidable in a project site, the ebonite lining has a flexible semi-ebonite bottom layer adhering to the metal to take up the mechanical shocks without passing the shocks to the hard ebonite lining layer above. In other words, an ebonite lining will have a 2-mm flexible ebonite bonded intimately with metal surface and 3 mm as a top layer resistant to corrosive media. Soft rubber linings will withstand temperature fluctuation as they are elastic and basically shock absorbing.

In road tankers, many times a change over of chemicals is a common practice, since it is not economical to keep tankers for each type of corrosive acids / chemicals. In this case, it is advisable to rinse the tank with water before filling up different chemicals each time. In general, the transportation tankers such as railway tanker, road tankers and ship tankers have dimensions which can still be vulcanized in autoclaves. In this kind of shop lining, there is no limitation concerning the choice of rubber compound types. Due to outside influences such as forces connected to fluid flow and jerks in the tank, dynamic stresses occur on all transportation tankers. In addition to this, as said earlier change of chemicals loaded in the tankers are often made by operators. In general, it can be said that the lifetime of the lined tanker is shortened with frequent change of chemicals. The most commonly handled acids in a single tanker can be hydrochloric acid, phosphoric acid, dilute sulphuric acid, caustic soda lye, hypochlorite, formic acid, dilute hydrofluoric acid, residual acids from pickling tanks, and regenerated acids.

4.16 Inspection of Rubber Lining

Pinholes in a rubber-lined tank will expose the underlying metal surface to corrosive chemicals, which are handled by the tank. Continuity of rubber lining is checked with a spark tester with a voltage varying from 6000 to 20,000 V, depending on the thickness of rubber and also the conductive property of the lining compound. While using the spark tester, it is necessary to ensure that the spark does not remain continuously in one spot, to ensure that a burnt hole does not occur through the lining material, because of the continuous sparking.

4.16.1 Rubber Lining of Large Storage Tanks

Rubber lining of large storage tanks is a challenging job and the procedure involved embraces all aspects of multidisciplinary engineering practices, such as chemical, mechanical and electrical. Typical rubber lining procedure for a phosphoric acid storage tank situated in a receiving port terminal is described below.

Huge circular storage tanks are normally rubber lined with precured rubber sheets using self-curing bonding adhesives, at the tank site. The site humidity is checked to be at not more than 65, since high humidity will interfere in the effective bonding of the lining with the metal surface. The lining operation is preferably stopped if rain prevails. In the case of a phosphoric acid storage tank, either a natural soft rubber, neoprene rubber or butyl rubber of durometer hardness 50–55°A is used respectively, depending on the defoaming agents or any additives in low concentration in the bulk acid. The adhesive used will be a neoprene based one with an isocyanate based accelerating agent for self-curing. The tanks installed in terminals normally will have a diameter ranging form 20 m to 30 m and height from 9 m to 15 m. The lining thickness normally used in practice is 3 mm for roof, 5 mm for shell and 10 mm at the floor. For tanks of height above 20 mm, a multistage, normally six-stage scaffolding of approximately 1-1/2 to 2 m height between stages is erected inside the tank.

In such huge tanks, since the area to be rubber lined is more than 2000 sq meter including pipes and fittings, manhole flanges and blind flanges and other accessories, the total area is sand blasted, primer coated and rubber lined in stages. Before sand blasting the tank is to be inspected for good metal surface free of pittings and weld projections which are to be ground smooth especially at joints. The various steps of lining involve, sheet cutting, sand blasting, adhesive coating and sheet laying. The sheets are cut to the required size with taper cuttings at ends of joints. On the blasted surface three coats of the adhesive bonding solution is applied with adequate drying time between coats. The final coat will have the isocyanate accelerator admixed with neoprene based adhesive. After drying, the sheets are laid and rolled down with a roller eliminating the air.

In the tank, the sheet joints at the roof and at the floor level should be as shown in figure 4.1. At the floor, the sheet end from the shell

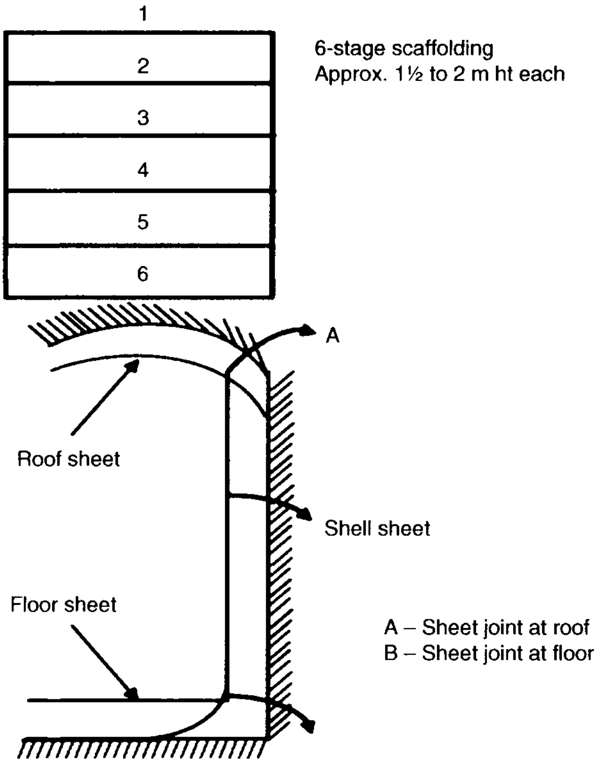

Figure 4.1 Schematic diagram showing sheet joints at roof and floor of tank.

Lining Thickness: Roof Thickness 3 mm
Shell Thickness 5 mm
Floor Thickness 5 + 5 = 10 mm
Shell 2nd layer up to 1 m ht 5 + 5 = 10 mm

should be laid below the floor sheets, and not otherwise, and the sheet end at the roof should be laid beneath the shell sheet and not otherwise. A 1-mm security strip 50 mm wide should be laid on the joints.

4.17 Sheet Dimensions

When the rubber sheets are handled and hung during the lining operation done on the shell vertically there is a stretch of about one cm per meter of length of the sheet due to self-weight and rolling, i.e., for a 10-m sheet when vertically laid, the stretch will be 10 cm. The stretch in a shorter sheet less than 2 m long is not significant. The stretch of the sheet is more for low hardness compounds. (45 to 50°A). However, the practical hardness of a sheet for such precured lining should not be more than 60°A. Each length of sheet for cutting to size is determined taking into consideration the stretch as well as the overlap joints which are staggered. This stretch factor should be taken into consideration before laying to avoid undersize or oversize.

4.18 Sheet Laying and Rolling

The following procedure is followed normally in practice:

Mark the horizontal reference line on the tank surface.
Lift the sheet to the first stage in the scaffolding.
Fix one end lengthwise on the horizontal reference line simultaneously fixing the other end.
The rubber sheets are also coated and dried prior to laying with the primer coat of the adhesive solution.
Roll down from the top reference line with a 2″ roller, eliminating the air between the metal and the sheet. From any point the rolling should be started from centre, side wise and downwards, eliminating the air. The overlap joints should be re-rolled finally. The sheets should be segmented by marking with a chalk stick, each segment being marked after rolling to differentiate rolled as well as unrolled surfaces.

Procedure of tank inspection before undertaking the lining operation

After the fabrication of the tank, the metal surface should be inspected for any pittings or projection and the same is to be leveled out by grinding.

This visual inspection should be done before the tank is hydraulically tested since rusting formed immediately after the hydraulic test will camouflage the defects on the surface.

Any leaks at the metal joints found during hydraulic testing should be repaired before the start of rubber lining and not during the operation.

Before the start of rubber lining, the tank should be earthed properly. The lining operator should check the earthing beforehand.

4.19 Lining Procedure for Pipes

In the case of pipes, the sand blasted inner surfaces are coated by pouring of the adhesive solutions. For this purpose the pipes are laid obliquely on two A frame stands of different height say 3′ and/or 2-1/2′. The adhesive solution is then poured through the pipe, which during this operation is rotated slowly and the excess is collected in a container at the opposite end. This operation is repeated twice in each case, the coating of the adhesive solution being allowed to dry. Then a previously formed tube of rubber having length of at least 50 cm longer than that of the pipe is closed at both ends. At one end a small opening is made by pinching and the tube is inflated with air. The tube is then drawn into the coated pipe with the aid of a rope made of nylon or cotton duck. The air pressure is then increased by additional pumping of air through the pinched hole to allow the tube to be pressed well on the wall of the pipe. The two closed ends of the tube are then cut open and one of the protruding ends is folded and pressed into contact with the whole area of flange of the MS pipe. The other end of the pipe remains free when the MS pipe is firmly clamped. A bell shaped rubber bung of low hardness (35°A to 45°A) is slowly drawn into the pipe from the end where the rubber is folded and fixed on to the flange by means of a cable attached to an electric pulling winch motor. The diameter of this rubber bung is about 10% greater than the inside diameter of the pipe to be lined and is coated with lubricants such as talc, soft soap to reduce the friction when it is drawn through. When the bung thus moves it presses the rubber tube against the wall of MS pipe and expels the air trapped between the tube and the MS pipe. Finally the free end of the tube is then pressed onto the other flange with a roller and stitched well. The lined pipe is now ready for autoclave vulcanization.

4.20 Storage of Rubber Lined Pipes

The following precautions are to be taken while storing rubber lined pipes prior to erection and commissioning.

The outside surfaces of the rubber lined pipes should be protected against atmospheric corrosion, such as rusting with an anticorrosive weather resistant coating based on chlorosulphonated polyethylene or neoprene. A primer coat of red oxide is given. In many installations, epoxy coating or chlorinated rubber based coating also is applied if cost considerations are not significant. It is, however, recommended that a suitable white paint is applied on the outer surface as the same will reduce the heat transmitted on rubber lining and the adhesive bonding beneath it.

The pipes should be stored in stands at least about 3 ft above ground level for handling without damage. The pipes should be covered with tarpaulin if stacked outdoors and free air flow should be ensured to avoid hot air packets, to prevent premature oxidation.

It is advisable to avoid direct exposure to the sun, and other climatic conditions should be avoided. However, in huge tanks in port terminals, this is not possible and therefore a weather resistant coating is given.

The ideal measure will be that the rubber lined surface is always kept wet with water in order to arrest the likely deterioration from ultraviolet rays and ozone attack during storage.

4.21 Design and Fabrication of Lining Supports for Handling Lined Equipment

Before lining is carried out on the equipment the important points and precautions to be considered and taken care of are:

- The metal surfaces must be accessible for manual working. Suitable manholes and gateways are to be provided in the structures for movement of operators and for adequate ventilation.

- Weld seams should be continuously smooth, and free from porosities and blow holes, projections and burrs. These should be smoothened out by grinding. See figure 4.2 below.
- Large tanks should be suitably reinforced outside arresting any deflection due to loads applied during application of lining.
- Settling allowances during fabrication and erection of the tankages should have been already taken care of before application of lining.
- Since electrical gadgets like exhaust fan, blowers, spark testers, etc. will be used during application of lining, the tanks should be properly earthed.
- The scaffolding inside the tank should be freestanding and not supported by the walls of the tank.
- The surface area being large in the huge storage tanks, it must be sand blasted and primer coated in sections.
- Suitable fire fighting devices should be placed inside the tanks, since the solvents handled in the lining application and coating adhesives are highly flammable.

Figure 4.2 Grinding of weld seams in a duct before shot blasting and coating of adhesive.

The fabricator of vessels is well informed in advance that the vessel is meant for lining and should be asked to follow the standard procedure for fabrication of equipment meant for rubber lining. The standard procedure generally contains the precautions to be taken for obtaining a good surface finish, welding finish and ease of accessibility of the fittings. nozzles, vents, piping etc. The lining contractor makes detailed guidelines to help the fabricators in the design and fabrication of tanks suitable for rubber lining.

To obtain a good lining, it is necessary that the lining surface either of mid steel, cast iron, stainless steel, aluminium, concrete, wood etc. should be fabricated / constructed avoiding sharp corners or edges. Sharp corners should be ground to have radius and the weld seams have to be ground flush. There must be accessibility by hand to all the surfaces to be lined. These criteria need not be applied to the lining of long pipes. In the case of long pipes, soft rubber bung of hardness 35°A is used as a tool for lining. However, spiral welded pipes lead to poor quality lining since the travel of the bung through the same will not be uniform and total air elimination cannot be guaranteed.

The welds should not be porous or should not have any cracks. As the lining is usually subjected to vulcanization in autoclave at temperatures of 130°C to 150°C, the entrapped air inside the weld could expand and blow out the lining, necessitating repair work on the lined vessel.

4.22 Surface Preparation for Rubber Lining

The advent of the sophisticated protective rubber lining has brought about the necessity of acquiring a wider knowledge of precise end conditions that must be fulfilled at the metal surface in order to achieve the utmost adhesion and bonding of the lining material to the metal. The performance of any type of lining is very much dependent on the cleanliness of the surface. The environment in which the equipment, storage tanks or road tankers are located determine to a great extent the type of lining that should be specified; for example a tank that is located in a harbour terminal will have to be rubber lined adopting precured rubber sheets with a self curing adhesive bonding solution. If maximum life expectancy of a rubber lining is expected, it should be firmly adhered to the metal. The key to the life and effectiveness of lined equipment exposed to a corrosive environment is its design and construction. The design and construction not only include the structural design enabling manoeuvrability during lining operation, but also the surface preparation. Proper surface preparation plays a vital role in the ultimate protection against corrosion. For film formation of the adhesive coating of even thickness all over and for uniform wetting and drying, removal of surface contaminants is all that is required.

4.23 Methods of Surface Preparation

Several methods are in practice for preparing the metal surfaces before rubber lining such as follows:

Cleaning with hand tools
Cleaning with power tools
Cleaning by sand blasting
Cleaning by water blasting and
Cleaning with steam, high pressure water and chemicals
Pickling with acid

Cleaning by hand tools is the oldest process. Today this is employed only when power tools are not available and where the surface is inaccessible to power tools and too small. The generally used hand tools are wire brush, scraper blades and chipping hammer and emery or sand paper. Hand held electric or pneumatic power tools for cleaning include sanders, pneumatic scalers, needle gun and rotary steel brushes.

Sand blasting is the cheapest method and widely used. Sand blasting is done using compressed air at an output pressure of 6 kg/cm^2. Low pressure reduces blasting efficiency considerably. Sand blasting is by far the best and most practical method, and for large areas, this is the method followed. For outdoor blasting operations coarse river sand is used for. For indoor blasting steel shots are used in closed shot blasting chambers which are rubber lined, see figure 4.3 below.

The high and the low points of the blasted surface called the "peaks and valleys" is an important factor for anchoring of the adhesive coating. The sand blasting nozzles generally in use will have either 1/4" 5/16" or 3/8" diameter. Where sufficient air is available at the correct and uniform pressure, the larger sized nozzles are preferred to smaller ones for more area coverage. The sand blasting operation can be continuous or intermittent. For continuous sand blasting, flow of sand should be continuous. For rubber lining of large storage tanks, sand blasting is done intermittently,

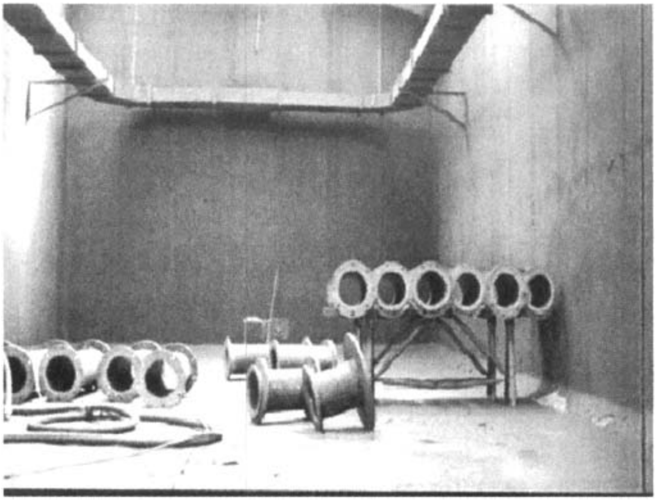

Figure 4.3 Rubber lined shot blasting chamber-shot blasted pipe fittings ready for adhesive coating.

simultaneously followed by primer coats. For productivity, the sand blasting equipment may have double hopper arrangements at some places.

Blasted surface qualities are often specified by users of rubber lined equipment. A white surface finish after blasting corresponds to a Swedish standard Sa3 or BS standard 4232 and to first quality. This white finish is defined as a surface with a grey white, uniform metallic colour slightly roughened to form suitable anchor pattern (peaks and valleys) for primer coat and subsequent lining. The finished surface should be free of all oil, grease, dirt, visible mill scale, rust corrosion products, oxides or remaining adhesive or paint coatings or any other foreign matter.

A near white surface finish corresponds to Swedish standard Sa 2-1/2 or BS4232 second quality. This finish is defined as one from which is removed all oil, grease, dirt, mill scale, rust, corrosion products, oxides remaining coatings, except for a very light shadows of light streak discolouration. At least 95% of the surface shall have the appearance of a white metal surface finish and the remainder shall be limited to light discolouration.

A commercial blasted surface finish corresponds to Swedish Standard Sa2 third quality. The finish is defined as one from which oil, grease, dirt, rust-scale and foreign matter have been completely removed from the surface, except for slight shadows, streaks or discolouration and pittings. In the case of old tanks, the surface might have been pitted, allowing slight residues to settle at the bottom of the pits. These should be removed by brushing.

Water blasting will remove substances such as loose and blistered paints, loose rust, grease and other accumulated residue. Although water blasting will not produce a surface equivalent to that produced by sand blasting, it is nevertheless an economical method of cleaning for lining application.

Cleaning with steam, hot water using chemical additives is adopted in connection with other methods. This method is known as "sweating". For example preparatory to relining of a tank handling caustic soda for its service life, it is a good practice first to thoroughly clean with steam or high pressure hot water before sand blasting. A 5% by weight of phosphoric acid solution in water added to the steam or high pressure water will neutralize any alkali residues. Care should be taken by the operator to avoid exposure to fumes and spillage, and standard precautionary methods and measures should be followed strictly. At times authentic information as to the use of acidic water handling in cleaning operation is not provided by the equipment suppliers. In this case, without seeking expert advise, such cleaning operation should not be resorted to. Pickling is done for cleaning the surface of small metal parts using dilute hydrochloric or sulphuric acids in pickling tanks which are rubber lined. The acid pickling process will yield a fresh metal surface suitable for bonding with rubber for manufacturing metal rubber bonded components. This process is followed mainly in the manufacture of rubber bonded components.

4.24 On Site Rubber Lining

Huge tanks are required to be rubber lined and vulcanized at the client's site because of limitations of transporting such tanks and many tank installations are outdoors in harbour terminals. It is necessary therefore to have good rapport and understanding with the client factory's engineers and their industrial environment to complete the rubber lining project successfully. It is necessary to identify problem areas which might affect the lining and the curing process without deviating from minimum work quality standards. Sharing of technical information such as duty conditions, availability of facilities such as electricity, air, water, and steam and other utilities is essential. Service conditions can range from atmospheric temperature to 120°C. The concentration of acids can range from 20% to over 70%. The medium may be under pressure or full or partial vaccuum. Sometimes tanks at the client's factory may be reaction tanks. The following steps may be helpful for accomplishing a successful rubber lining project. All service conditions must be considered when selecting the type of rubber lining. The factors to consider are:

- Compound design and compounding ingredients.
- Acid characteristics.
- Temperature in service, vacuum service or static storage.
- Solids in the system.
- Heating system in the tank.
- Defoamer type or other additives.
- Experience of rubber lining applicator.
- Safety system required.
- Rules and regulation of worker's union of the client factory.
- Any mandatory hours of work stipulated which might affect drying time.
- Schedule for completion.
- Client's plant entrance and exit rules.
- Any limitations on the use of plant resources and utilities such as steam, air and water.
- Whether any dehumidification equipment is available at client's site.
- Acceptance and rejection criteria of rubber lining.
- Availability of handling equipment.
- Availability of extra blind flanges for hot water curing
- Scaffolding.
- Type of blasting required whether sand blasting or shot blasting.

5

Rubbers and Their Relevant Properties for the Chemical and Mineral Processing Industries

5.1 Historical Aspects

Rubbers or elastomers have been used in the processing industries since the 19th century. They are used cost effectively, mostly because of their resistance to wear, impact, flexing and corrosion and also for their ability to control vibrations and noise. Rubbers are used reliably in process operations from mining, comminution, separation, reactions, through final product handling. The most appropriate rubber for a given application in mining and chemical processes is selected for its particular properties.

The property of elastic recovery of rubbers allows them to be used for many products which are subjected to deformation, whether by tension or compression, and must not be destroyed by such forces. Abrasion and corrosion resistances are often the main properties in choosing an elastomer-based product over alternative products. In the mineral processing industry, abrasion often results from a slurry's suspended particles coming in contact with an elastomer surface in a combination of impinging and sliding actions. The erosive wear of a metal or its alloy depends on its microstructure and hardness. An elastomer's resistance to abrasion especially for the impinging type depends on the resilience of the elastomer. When a particle with a small size contacts the wear surface with a moderate speed, the rubber deflects and then returns to its original position with little or almost no wear at all. This unique property of elastomers gives them a substantial increase in resistance to abrasion over metals.

Another main reason for using an elastomer product is its amazing chemical resistance. In general, the rule "like dissolves like" applies. This means non-polar elastomers such as natural rubber will handle most chemicals used in the mineral processing industries, which are typically water-based polar solutions or slurries. When non-polar solvents, corrosive chemicals such as acids and alkalies or oils are encountered, rubbers such as acrylonitrile butadiene, neoprene butyl and EPDM must be used. Field experience collected over several years can provide the best basis for successful material selection. Chemical resistance charts by suppliers of rubbers and chemicals are also useful. In difficult cases, especially those involving mixed and/or unknown chemicals at varying temperatures, immersion testing in the actual process plant is the best basis for the choice of the correct material of construction from among the multifarious types of rubbers and their compounds.

Most elastomers used in chemical and mineral processing are also used as composites. They can be bonded to textile fibers such as nylon, polyesters, polyaramides and others to increase strength and stiffness, with a loss in elongation. They can be bonded to metals to combine the rigidity and the strength of the steel equipment with the elasticity and corrosion and wear resistance of the rubbers. Rubber lining of the mild steel equipment and pipes with a special adhesive is a highly technical process, mostly being mechanically as well as manually carried out. An elastomer compound development is usually a compromise which can be shown as an equilateral triangle, the three Ps as shown in the following figure 5.1.

The rubber compounder tries to achieve the best compromise by choosing the elastomer or blends of elastomers and then adding various fillers and chemicals of which there are an almost infinite number of combinations. The mineral and chemical processing engineers

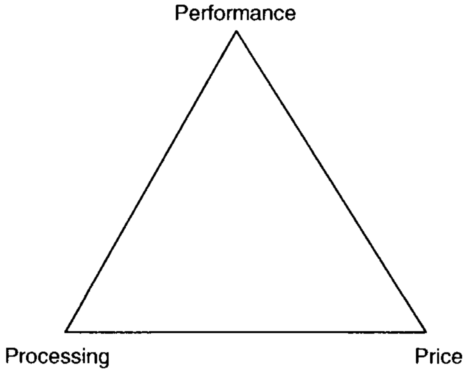

Figure 5.1 The 3Ps.

see only the performance and price part of the triangle, but the rubber chemist has to deal with the processing through compounding, mixing and forming such as calendering, extrusion, molding, hand lay-up methods of forming and the vulcanizing steps.

Ancient American people in the regions of Central Mexico extending south and east, including parts of Guatemala, Belize, Honduras and Nicaragua were processing rubber by 1600 BC. Christopher Columbus was probably the first European to see natural rubber. The mention of rubber trees is to be found in the eighth decade of *De Orbe Novo* by Pietro Martire d Angliera published in Latin in 1516 [1]. Very little use of rubber was made until 1823 when Charles MacIntosh patented the use of coal tar to dissolve natural rubber and used it to produce waterproof garments. In 1839 Charles Goodyear discovered vulcanization of rubber. In 1843 Thomas Hancock took out trials similar to the vulcanization techniques of Goodyear and was commercially more successful than Goodyear. One of his products such as thin rubber sheets were said to have been used in some form in the mineral processing industry. Goodyear's experiments of rubber with nitric acid aimed at discovering the stiffness of rubber which later was achieved by sulphur vulcanization, can be considered as a forerunner to the study of chemical resistance of rubbers. By 1850, a wide range of rubber articles were developed and although there is a doubt that they were not designed specifically for process industries, many products such as sheets were useful in the mineral and chemical processing industries as the rubber's elasticity and resilience and wear and chemical resistance were curious properties having relevance to the process plant and equipment and satisfying their requirements. According to Rubber Manufacturers Association, 1975, Washington DC USA, rubber lining of chemical process vessels was done in 1929.

Advances in rubber technology have been continuous since the early discoveries because of the curiosity it evoked. Most discoveries of wear and abrasion were made with the tyre industry in mind, as it was the largest consumer of rubbers in the civil and military transport systems during the first and second world wars. Since many of these advances involved basic properties such as abrasion, tear and flex resistance, these could be readily adopted by rubber chemists who were designing products for the chemical, fertilizer, mineral and ore processing industries. The high strength of natural rubber can be attributed to its ability to undergo strain induced crystallization.

5.2 Elastomer Types According to American Society of Testing Materials-ASTM D2000

ASTM D2000 is the standard classification system for rubber products in automotive applications. It also serves the needs of other industries in arranging rubber products into characteristic material designations. These designations are determined by types based on resistance to heat ageing, and classes based on resistance to swelling in oil. D 2000 is the more common tool among rubber manufacturers. The categorization of some of the more common types used in mineral and other processing industries can be found in ASTM D1418-01.

5.3 Mullins Effect

Natural rubber exhibits unique physical and chemical properties. Rubber's stress-strain behavior exhibits the Mullins effect and the Payne effect. It strain crystallizes. Under repeated tensile strain, many filler reinforced rubbers exhibit a reduction in stress after the initial extension, and this is the so-called Mullins Effect which is technically understood as stress decay or relaxation. The phenomenon is named after the British rubber scientist Leonard Mullins, working at MBL Group in Leyland, and can be applied for many purposes as an instantaneous and irreversible softening of the stress-strain curve that occurs whenever the load increases beyond its prior all-time maximum value. At times when the load is less than a prior maximum, nonlinear elastic behaviour prevails [2].

Although the term "Mullins effect" is commonly applied to stress softening in filled rubbers, the phenomenon is common to all rubbers, including pure gums which are compounds without filler loading. As first shown by Mullins and coworkers, the retraction stresses or decay of stresses of an elastomer are independent of carbon black when the stress at the maximum strain is constant. Mullins softening is a viscoelastic effect, although in filled rubber there can be additional contributions to the mechanical hysteresis from filler particles debonding from each other or from the polymer chains.

5.4 Payne Effect

The Payne effect is a particular feature of the stress-strain behaviour of rubber, especially rubber compounds containing fillers such as carbon black. It is named after the British rubber scientist A. R. Payne, who made extensive studies of the effect in 1962 [3]. The effect is sometimes also known as the Fletcher-Gent effect [4] after the authors of the first study of the phenomenon in 1953. The effect is observed under cyclic loading conditions with small strain amplitudes, and is manifest as a dependence of the viscoelastic storage modulus on the amplitude of the applied strain. Above approximately 0.1% strain amplitude, the storage modulus decreases rapidly with increasing amplitude. At sufficiently large strain amplitudes (roughly 20%), the storage modulus approaches a lower limit. In that region where the storage modulus decreases, the loss modulus shows a maximum. The Payne effect depends on the filler content of the material and vanishes for unfilled elastomers. Physically, the Payne effect can be attributed to deformation-induced changes in the material's microstructure, i.e., to breakage and recovery of weak physical bonds linking adjacent filler clusters. Payne effect is essential for the frequency and amplitude-dependent dynamic stiffness and damping behaviour of rubber bushings, automotive tyres and other wear and abrasion resistant products for the minerals and fertilizer slurry handling industries.

In the design of rubber as a material of construction to meet specific application requirements, the engineer has to first understand the limitations of the physical and functional properties of the rubber material, in order to avoid using the same, to stresses (applied loads) and strains (deformations) that exceed these limits. The important point to be understood is that the strengths of rubbers are considerably lower than those of metals, plastics or wood. Yet the elasticity of rubber is the one major property which is of paramount importance, when compared to non-rubbery materials. The rubber's ability to return to the original shape and dimensions after a deforming force is removed is often called resilience and memory. Resilience implies quick return while memory implies slow return just as in raw unprocessed and unvulcanized rubbers which are subjected to certain stresses. For wear and abrasion resistant requirements resilience is important because it allows the rubber to adapt to variations in the impinging as well as sliding forces on its surface. Memory which implies a slow return is nothing but creep.

5.5 The Reversibility

The reversibility of the elastic deformation of the rubber is known as hysteresis. For a given elongation before the ultimate breaking elongation, the stress is relaxed and the sample is allowed to retract and the retracting energy is lower than that used for stretching. This phenomenon is hysteresis [5]. Thus hysteresis, reflecting Mullins effect, indicates that the energy recovered by the rubber during retraction is distinctly smaller than the energy used up in stretching. If a rubber sample is subjected to several successive stretches followed by retractions, and after cessation of the applied stress the rubber sample finally reaches a limit when the retracted length can be seen to be longer than the original unstretched length, this is called permanent set. For vulcanized rubber the permanent set is smaller and is also influenced by the compound formulation. Permanent set is a measure of elasticity of rubber. In some cases the permanent set is also determined during compressive stresses. For application of rubber in the mineral industry it has to decay or relax less and the permanent set has to be as low as possible, thus becoming quite suitable for impinging and sliding abrasive forces.

5.6 Resistance to Wear and Tear

The resistance to wear and abrasion of a rubber when in contact with the moving ore or fertilizer slury is related to other physical properties such as hardness and tear resistance. Thermal stability and fluid compatibility and fatigue resistance also are associated with wear resistance. Vibration and pulsation in a process system or pipelines are common occurrences in chemical process industries which lead to increased attack of corrosive fluids on the surface. The vibration fatigue would be an unavoidable factor which is aggravated further by improper installation of the moving system. These pulsations are reduced by the installation of flexible rubber expansion joints to a greater extent. In iron ore mines, the concentrated ore is made as a slurry in the concentrator plant and transported to pelletising plants through long distance pipelines. These pipes having no flanges are joined with victaulic couplings which are recent improvements fixed on grooves in the pipe ends. These couplings are made of rubber materials which prevent leakage of the slurries which have the required density enabling the flow through the pipes. The slurry is transported under high pressure to pelletising plants and other destinations. The rubber ring gaskets installed in the coupling play a vital role in preventing leakage of the slurry. In such cases the rubber is required to withstand highly abrading ore particles and should have high cut and tear resistance.

5.7 Chemical Compatibility

Chemical compatibility is another important factor to reckon with in material selection as in the case of butterfly valves which are frequently used in industrial fluid flow systems where the valves are operated to load and unload different kinds of fluids for shipment or storage. These applications include tank trailers for transportation of fluids from one location to another as well as fluid flow pipelines. A typical butterfly valve usually incorporates a resilient rubber seal component which the valve pivots to seal off the flow lines and when opened allows the fluid to be conveyed to the flow line. The chemicals transported in tanks using butterfly valves are often caustic or acidic. These chemicals corrode the pivot area of the valve making its function ineffective. The rubber gasket material prevents leakage while the valve chamber is protected by a chemically resistant rubber material.

Rubber manufacturers develop their own rubber compounds suitable for constructing chemical plants and equipment possessing the chemical and physical properties to match the functional requirements and duty conditions of the application. The rubber compounds used in the manufacture are derived from base rubbers such as natural rubber, nitriles, neoprenes, butyls, styrene butadiene, carboxylated nitriles, viton, silicones and polytetrafluoroethylene. Of all the properties exhibited by the various types of rubber compounds, the most critical ones pertain to how they change when they are used in application as construction material and while in service. Every physical property changes with age, temperature, pressure, vacuum and other factors which can include corrosive chemicals such as acids, alkalies, salt solutions as well as fumes and gases. Compounds with the least tendency to change their properties whether chemical or physical are easier to work with. More adaptable and versatile products can be produced with these compounds.

5.8 Glass Transition Temperature

When different elastomers are being described, a fundamental property which is often quoted is the glass transition temperature, Tg, which differs from one elastomer to another. For example, for natural rubber Tg is –70°C (–95°F). Broadly this means that above –70°C the material behaves as a rubber, but below –70°C the material behaves more like a glass. When glassy, natural rubber is about one thousand times as stiff as it is when rubbery. When glassy, a hammer blow on natural rubber will cause it to shatter like a glass; when rubbery the hammer is likely just to bounce off.

At normal temperatures, the rubber molecular chains are in a constant state of thermal motion, they are constantly changing their configuration, and their flexibility makes them reasonably easy to stretch. It is to be noted that as the temperature is lowered the chains become less flexible and the amount of thermal motion decreases. Eventually, a low temperature, the glass transition temperature, is reached, where all major motion of the chains ceases. The material no longer has the properties which make it a rubber, and it behaves as a glass.

For all practical engineering uses of rubbers we require good flexibility, and, therefore, it is essential that we use them only at temperatures which are comfortably above the glass transition.

This is generally no problem for natural rubber with a Tg of –70°C, or cis-butadiene rubber with a Tg of –108°C (–160°F). But many synthetic rubbers especially those which have been designed to be highly heat or oil resistant, have much higher Tgs, and this must be borne in mind when selecting them for service applications. For example some fluoroelastomers, which have excellent oil and heat resistance, have a Tg not far below normal room temperature. This can result in problems if a component which is required to work at high temperature also has to serve the same function on cooling down, and must be considered in design. The glass transition temperatures of various rubbers are given below.

Table 5.1 Glass-transition temperatures of various rubbers

Rubbers	**Tg °C**
Cis-1,4-polybutadiene	–105
Cis-1,4-polyisoprene	–70
Polyisobutylene	–70
Polybutadiene (emulsion polymerized; 20% 1,2)	–85
Polybutadiene (sodium catalyzed; 60% 1,2)	–46
Ethylene-porpylene copolymer (50/50)	–60
Poly(butadiene-co-styrene) 77/23	–56
Poly(butadiene-co-styrene) 64/36	–38
Poly(butadiene-co-acrylonitrile) 80/20	–56
Poly(butadiene-co-acrylonitrile) 70/30	–41
Poly(ethyl acrylate)	–22
Poly(n-butyl acrylate)	–56
Poly(n-octyl methacrylate)	–20
Polyester-urethane	–35 to –50
Polychloroperne (85% trans-1,4)	–45
Poly(perfluoroproypylene-co-vinylidene fluoride)	–55
Polydiemthylsiloxane	–120

5.9 High Temperature Behaviour

The limit to the upper temperature at which a rubber can be used is generally determined by its chemical stability, and will thus vary for different rubbers. Rubbers can be attacked by oxygen or other chemical agents, and because the attack results in a chemical reaction, its potency will increase with temperature.

Degradative chemical reactions are generally of two types. The first are those which cause breakage of the molecular chains or cross links, softening the rubber because they weaken the network. The second are those which result in additional cross linking, hardening the rubber - and often characterized by a hard, degraded, skin forming on the rubber component. Selection of a suitable rubber and the use of chemical anti-degradants can reduce the rate of chemical attack.

5.10 Fluid Resistance

The structure of an elastomer comprises a network of chains, meaning that there are gaps between adjacent chains. Indeed the elasticity of rubber relies on substantial thermal motion of the chains, which would not be possible if the chains were closely packed. The free volume available in the rubber means that some liquids can enter the rubber and cause swelling - sometimes very large amounts of swelling. For example the ability of oil to swell natural rubber is well known.

All rubbers and all liquids have specific values of solubility parameter, a knowledge of which enables designers to avoid excessive interaction between a rubber and the fluids which it will contact in service.

Solubility parameters were developed by Charles Hansen as a way of predicting if one material will dissolve in another and form a solution. They are based on the idea that "like dissolves like" where one molecule is defined as being like another if it bonds to itself in a similar way. The Hildebrand solubility parameter (δ) provides a numerical estimate of the degree of interaction between materials, and can be a good indication of solubility, particularly for non-polar materials such as many rubbers. Materials with similar values of solubility parameters are likely to be miscible [7].

5.11 Incompressibility

Another property of rubbers which distinguishes them from other solid materials is their incompressibility. For most practical purposes, other than use under very high pressures, elastomers do not change their volume significantly when deformed. A rubber band may stretch 600%, but if its volume were measured in the stretched state it would be found to be almost identical to its unstretched volume. This has important implications for designing with rubbers as the stiffness of components can be controlled, not only just by altering the stiffness of the rubber itself, but by various geometrical designs. This phenomenon, known as shape factor effects, is described in more detail in standard textbooks, and leads to great versatility in design. In particular it enables engineering rubber components as well as rubber bonded metal shock mounts to be designed with different, and controlled, stiffness.

5.12 Natural Rubber

Natural rubber is a polymer of isoprene - most often cis-1,4-polyisoprene - with a molecular weight of 100,000 to 1,000,000. Typically, a few percent of other materials, such as proteins, fatty acids, resins and inorganic materials is found in natural rubber. Polyisoprene is also created synthetically, producing what is sometimes referred to as "synthetic natural rubber". Owing to the presence of a double bond in each and every repeat unit, natural rubber is sensitive to ozone cracking. Some natural rubber sources called gutta percha are composed of trans-1,4-polyisoprene, a structural isomer which has similar, but not identical properties. Natural rubber is an elastomer and a thermoplastic. However, it should be noted that as the rubber is vulcanized it will turn into a thermoset. Most rubber in everyday use is vulcanized to a point where it shares properties of both, i.e., if it is heated and cooled, it is degraded but not destroyed.

The physical properties of natural rubber and synthetic rubber compounds are affected greatly by the type and amount of fillers used. Carbon black is the most commonly used filler. Increasing amounts of carbon black increases the hardness and modulus of the vulcanizates. Resilience and resistance to impinging type abrasion decrease along with elongation. Tensile strength and tear strength and resistance to sliding abrasion increase with increased loading up to a certain point and then decrease. The carbon black loading in the compound is adjusted to maximize the desired and matching properties required for the mineral processing equipment. Fine particle sized silica fillers can also be used with more or less the same response as carbon black. The relatively recent highly dispersible forms of silica in combination with organosilicone coupling agents are the basis for green tyre tread which gives good abrasion resistance along with low rolling resistance. These advantages pertaining to the technology of tyres can also be used to produce compounds suitable for manufacture of construction materials and other composites for the mineral processing industry. In NR compounds for the mineral processing industry, this technology in tyre compounding can be used to produce compounds with abrasion resistance of a "pure gum" compound and with a cut and tear resistance of a harder carbon black loaded compound. In application such as mill circuit discharge pumps handling slurries with up to 12-mm diameter particles, the service life is increased considerably for the pump liners in the mineral processing. The favourable elastic properties of NR manifest themselves in very low damping (hysteresis) and low heat buildup in dynamic deformation. This makes NR especially suitable in dynamic applications such as vibration elements used in centrifuges and most importantly in very large off-road tyres in the mining site which also use mostly NR because of its low heat buildup, dynamic fatigue resistance and excellent resistance to cutting and chipping.

NR vulcanizates are not as heat resistant as most synthetic rubbers; 70°C is normally considered the maximum service temperature in dry application. Special compounding techniques using very low or no sulphur cure systems along with protecting antioxidants can extend this limit to over 90°C especially in wet service such as slurry handling pipes and equipment such as launders, chutes etc. Unprotected NR compounds are very prone to ozone cracking especially in non-black compounds. If such compounds are stored improperly under stress, they may even crack before being put into service. Black compounds which contain proper amounts of wax and staining antioxidants are far less prone to cracking.

Since NR is non-polar, its vulcanizates can swell to several times their original volume in non-polar solvents such as mineral oils, toluene, gasoline and diesel oil. It has good resistance to polar fluids such as mild acids and bases typically encountered in the mineral and chemical processing industries. The compression set resistance

Oil Resistant Natural Rubber Formula

No.	Ingredient	Phr
1.	RMA 4	100.00
2.	Antioxidant	1.00
3.	Zinc Oxide	5.00
4.	Lamp Black	300.00
5.	Sulphur	3.00
6.	MBTS	1.50
7.	Stearic Acid	2.00
8.	Process Oil	3.00

Curing time 10 to 15 minutes at 153°C
Shore hardness : 65°A

at relatively low temperatures (< 70°C) of NR can be very good with suitable compounding with low sulphur addition. The low compression set property makes it useful in load bearing applications in bearing pads and engine mounts. The low temperature properties of natural rubber vulcanizates are excellent without any special compounding and the same can be increased to a larger extent by admixing small amounts of silicone and polybutadiene into a NR compound. NR can also be blended with various other synthetic rubbers to improve heat resistance, sliding abrasion resistance and moderate oil resistance. NR is added to other synthetic rubbers to improve building tack and green strength and also to lower the cost of synthetic rubber based compounds. Before the advent of specialty synthetic rubbers such as nitrile and neoprenes, natural rubber compounds were actually used for materials requiring moderate oil resistance. An olden days' oil resistant natural rubber compound is given above for reference. One can observe the high loading of softer carbon black resulting in low rubber content which accounts for moderate oil resistance.

5.13 Synthetic Polyisoprene (IR)

Initial attempts to make synthetic rubber similar to NR date back to mid 1800s. Modern synthetic polyisoprene is designed to be similar to natural rubber in structure and properties. Although it has lower green strength, slower cure rates, lower hot tear, and lower aged properties than its natural counterpart, synthetic polyisoprene exceeds the natural types in consistency of product, cure rate, processing, and purity. In addition, it is superior in mixing, extrusion, molding, and calendering processes. This rubber does not require much mastication. The higher cis-1,4 configuration of this polymer closely resembles the properties of natural rubber and is the most important commercially. Modern synthetic polyisoprene is designed to be similar to natural rubber in structure and properties. In addition, it is superior in mixing, extrusion, molding, and calendering processes.

The successful synthesis of stereoregular polyisoprene (IR) fulfilled a goal sought by polymer chemists for nearly a century. Researchers knew that isoprene was the building block for natural rubber, and through the years, many attempts were made to synthesize materials with similar properties. Initially, the resulting polymers failed to exhibit some of the desired aspects of natural rubber because of differences in microstructure, which plays an important role in polyisoprene's physical properties. The polymer chains in the early synthetics contained mixtures of all possible molecular configurations joined together in a random fashion. Specifically, they lacked the very high cis-1,4 structure of the natural rubber backbone that gives it the ability to undergo strain crystallization.

In the mid 1950s, researchers discovered a kind of special catalysts called stereospecific catalysts which allowed realization of a nearly pure cis-1,4 structure in the polymerization, and in doing so, the production of a synthetic natural rubber having similar molecular configuration was obtained. Initial commercialization was realized in 1960 by Shell Chemical Company with the introduction of Shell Isoprene Rubber, produced with an alkyl lithium catalyst. However, the cis-1,4 content was insufficient to achieve the important crystallization properties of natural rubber. In 1962, Goodyear company introduced a Ziegler-Natta (titanium-aluminum) catalyzed IR with a cis-1,4 content of 98.5%, finally allowing the benefits of strain-crystallization to be realized. Goodrich-Gulf introduced another Ti-IR polymer about three years later, but subsequently withdrew it from the market in 1978. The manufacture of high cis IR has since been undertaken elsewhere, primarily in Russia and Japan.

The main reason that this rubber is not used in process industries in place of natural rubber could be that the price of this rubber is much more than that of natural rubber.

5.14 Styrene Butadiene Rubber (SBR)

As one of the most versatile copolymers in the world today, styrene-butadiene rubber is used in a number of different applications around the world. Some facts about the development of styrene-butadiene rubber and some of the products that are created with this strong and reliable synthetic rubber are described below.

Styrene-butadiene rubber, or E-SBR as it is known in manufacturing circles, was first developed in the 1930s. Known as Buna S, the compound was prepared by I.G. Farbenindustrie in Germany. Manufacturing styrene-butadiene rubber was through an emulsion polymerization process which produced a material that had a low reaction viscosity, yet had all the attributes of natural rubber.

One of the other advantages was that the production of SBR was very cost-effective. The synthetic rubber was competing with natural rubber resources, especially in the area of the manufacture of tyres, which at the time were still solid rubber. Other countries began to duplicate the efforts and by the dawn of the subsequent decade, many developed nations were in the business of producing SBR for use in a number of products.

The United States stepped up the production of styrene-butadiene rubber during World War II, as a means of augmenting the sacrifice drives to stockpile rubber for the war effort. Much of the production was done in plants owned by the government, and many of the products manufactured went directly to the armed forces that were fighting overseas. It was also during this time that a cold polymerized blend of styrene and butadiene was created that was superior to the older hot polymerized styrene-butadiene rubber that had been produced in years past. After the end of the war, the government began to sell off the SBR plants to private industry. It was known earlier as GR-S (Government Rubber-Styrene) in the US. By 1955, the production of styrene-butadiene rubber had passed completely from the hands of the US government and into the hands of many of the leading manufacturers around the country. It is a major rubber even today for manufacturing passenger and light truck tyres, but it is not much used in large off-road tyres in mining sites, since its compounds have higher heat build-up than natural rubber compounds and less resistance to cutting and tearing. It does have good resistance to sliding abrasion and impact and so it can be used in products such as beltings, sheet rubber, truck box liners, and mill liners in ore concentrator plants. The heat resistance is somewhat better than NR and special

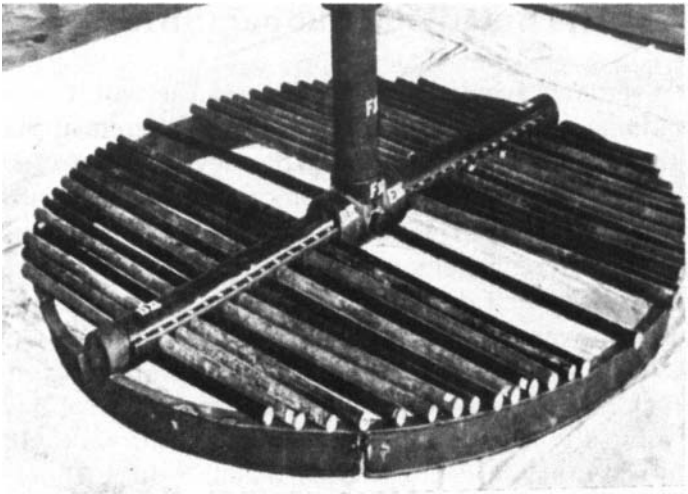

Figure 5.2 SBR ebonite internals assembled view.

Courtesy: Can C consulting India Chennai, India

compounding can take the maximum temperature rating to approximately 110°C. In the chemical process industry it is used as ebonite composition for pipe internals in chlor-alkali plants handling brine and wet chlorine. Assembled ebonite internals made from SBR ebonite used in a chlor-alkali plant for brine filter is shown in figure 5.2.

Processing of SBR is generally good, but it lacks the tack and green strength of NR. It has lower nerve and flows better than NR and can be blended with NR to improve flow . Styrene-butadiene rubber turns up in a number of products, some of them predictable and others that may come as a surprise. SBR is used today for auto tyres, including light truck tyres. Many companies that retread old tyres will use a styrene-butadiene rubber coating to produce the retreads as well. Among the other obvious uses are belts and hoses for chemical industries, gaskets and molded ebonite components for chlor alkali industries.

Because of its good abrasion resistance and good ageing stability when protected by additives, it is widely used in car tyres, where it is often blended with natural rubber. It was originally developed prior to World War II in Germany, but during the war it was used extensively by the USA to replace natural rubber supplies from the far-East, that had been captured by the Japanese. SBR with high styrene-content is hard. Since the glass transition temperature of butadiene is extremely low, it is not to be confused with a thermoplastic elastomer made from the same monomers, styrene-butadiene.

5.15 Butadiene Rubber

Most of the butadiene rubber used is solution polymerized with a very high cis-1,4 configuration. BR is seldom used as the sole polymer in any mineral processing application as its strength is very low and processing is very difficult. BR is most commonly blended with natural rubber or with SBR, most of such technology coming from the tyre industry, even though the abrasion mechanism of tyres on the roads is somewhat different from that of the rubber exposed to ore particles dry or wet. When blended with NR or SBR in compounds having fillers to give hardness usually in the range of 50 to 80 shore A, BR improves abrasion resistance, heat ageing, resilience, reversion resistance, fatigue resistance and low temperature flexibility.

Side walls of passenger car tyres are commonly based on blends of natural rubber and cis-4 polybutadiene. They have outstanding resistance to catastrophic crack growth under severe conditions such as when a tyre runs into a sharp edged stone, hits a deep chuck hole, and also a sidewall must resist crack growth over long times at smaller strains experienced during normal rolling. This resistance to different types of crack growth is very important for many products used in mineral and fertilizer processing other than tyres such as belts, especially those with flanges, hoses and mill liners which often use blends of NR and BR. The processing of BR blends is generally good. NR/BR blends have good tack and green strength, and so they can be used in structures requiring rubber composites.

Any fertilizer materials are minerals and have certain hardness values and therefore cause wear. Other plant nutrient salts or chemicals, particularly in the presence of moisture, will additionally produce corrosion. It is apt in this context to know some details of the scratch hardness of minerals which cause wear and abrasion, and this is normally measured in terms of Mohs scale [8].

The Mohs hardness scale was developed in 1822 by Frederich Mohs. This scale is a chart of relative hardness of the various minerals (1-softest to 10-hardest) See table 5.2 below. He selected the ten minerals because they were common or readily available. The scale is not a linear scale, but somewhat arbitrary.

Table 5.2 Moh's hardness of minerals

Mineral	**Hardness**
Diamond	10
Corundum	9
Topaz	8
Quartz	7
Orthoclase-white quartz	6
Apatite	5
Fluorite	4
Calcite	3
Gypsum	2
Talc	1

Mohs' hardness is a measure of the relative hardness and resistance to scratching between minerals. Other hardness scales rely on the ability to create an indentation into the tested mineral (such as the Rockwell, Vickers, and Brinell hardness - these are used mainly to determine hardness in metals and metal alloys). The scratch hardness is related to the breaking of the chemical bonds in the material, creation of micro fractures on the surface, or displacing atoms in the metals of the mineral. Generally, minerals with covalent bonds are the hardest while minerals with ionic, metallic, or van der Waals bonding are much softer.

When doing the tests of the minerals it is necessary to determine which mineral was scratched. The powder can be rubbed or blown off and surface scratches can usually be felt by running a fingernail over the surface. One can also get a relative feel for the hardness difference between two minerals. For instance, quartz will be able to scratch calcite with much greater ease than you can scratch calcite with fluorite. One must also use enough force to create the scratch (if you don't use enough force even diamond will not be able to scratch quartz - this is an area where practice is important). You also have to be careful to test the material that you think you are testing and not some small inclusion in the sample. This is where using a small hand lens can be very useful to determine if the test area is homogenous.

The effects of high hardness are important in many fields. Abrasives are used to form and polish many substances. Diamonds are an important mineral component in cutting tools for the manufacturing of metals and other substances, forming dies for the drawing of wires, and for cutting cores in oil wells and mineral exploration. Emery - a variety of corundum, is used in many abrasive products that do not require the hardness (or expense) of diamond tools. Garnets were used as an abrasive in sandpaper. Talc is an extremely soft mineral that has been used in bath powders (talcum powder).

Mineral hardness is also important in sedimentary rocks. Harder minerals tend to be able to travel longer distances down river systems. Quartz can often undergo several cycles of erosion, transportation and lithification (change of sediments to rock).

5.16 Butyl Rubber (IIR)

IIR is a copolymer of mainly isobutylene and a small portion of isoprene. This largely saturated isoprene chain determines butyl's main properties such as good resistance to oxidative and ozone degradation, to corrosive chemicals and low gas permeability. It is very non-polar and therefore resistant to polar chemicals, especially acids and bases at higher temperatures and concentrations when compared with NR compounds. Mechanical properties are good enough and resilience at room temperature is very low and this leads to low resistance to impinging abrasion. Its main use in mineral and chemical processing industries is in the lining of tanks and pipes and pumps. IIR is very incompatible with diene rubbers such as NR,SBR and BR. Small amounts of an IIR compound can contaminate other compounds and be contaminated by other compounds. Therefore, the manufacturing facility must be carefully created to avoid such contamination.

5.17 Chlorobutyl (CIIR) and Bromobutyl (BIIR)

These two rubbers are prepared by halogenation of the butyl. Halogenation gives increased cure reactivity. As a result, improvement occurs in vulcanization rates resulting in improved properties over butyl. The state of cure and reversion resistance and co-vulcanization with other diene rubbers can also be suitably monitored. CIIR and BIIR vulcanizates have lower gas permeability, better weather and ozone resistance, higher hysteresis, better resistance to chemicals, better heat resistance, better adhesion to other rubbers than those of IIR. CIIR and BIIR vulcanizates are used in much the same places as IIR and have replaced IIR in many applications such as belts, hoses and tank lining of digesters in rare earth and sand complex units. There is very little difference in the processing of CIIR and BIIR or IIR except that CIIR and BIIR do not contaminate or are contaminated by other diene rubbers.

5.18 Ethylene Propylene Rubbers (EPM and EPDM)

The first polymers commercialized were merely the copolymers of ethylene and propylene (EPM). Because the polymers are totally saturated, the compound could only be cured with peroxides. The limitations of peroxide cures did not satisfy the needs of the rubber industry. If a third monomer, a diene is introduced during polymerization the resulting rubber (EPDM) can be vulcanized with sulphur giving more flexibility in curing without a significant loss in the stability of the original copolymer. EPDM rubber is much more commonly and frequently used in the process industries. Since EPDMs have fully saturated backbones (the unsaturation of the diene is in the side chain), the resistance to ozone and oxygen is excellent. As non-polar hydrocarbon elastomers with an amorphous nature, EPDM rubbers have good electrical properties. The non-polar nature gives resistance to polar materials such as phosphate esters, many ketones and alcohols, many acids and bases, water and steam. Resistance to chlorinated solvents is fair enough. Resistance to non-polar oils, gasoline etc., is very poor although compounds with high loadings of carbon black and oil have lower volume swell, compared to other hydrocarbon elastomers.

Resilience of EPDM is not appreciable and so resistance to impinging abrasion is much less when compared with NR vulcanizates, but much better than butyl vulcanizates and as such butyl rubber has been replaced in many applications requiring such abrasion resistance. Resistance to sliding abrasion where shearing forces come into play is good as well as tear resistance. EPDM rubber is called as crackless rubber in chemical and mining industry circles because of its excellent resistance to tear. Compression set property particularly at high temperatures is good, if properly compounded.

Heat resistance of up to 200°C is achievable for special applications with proper compounding. Processing of this rubber is generally good except for the lack of building tack. This severely limits the use of EPDM in hand lay-up applications such as liners. However, with the use of proper solvents and adhesives this can be alleviated.

Since EPDM rubber is costly and the price fluctuates widely, high filler and oil loadings are resorted to, to achieve relatively low cost compounds. But these compounds tend to have poor strength and abrasion resistance. High quality stocks, especially those with peroxide cures, are considerably more expensive than NR, BR or SBR stocks. EPDM is used in belts and hoses meant for conveying hot materials because of its excellent heat resistance. Its excellent chemical resistance makes it a preferred rubber for specialty belts, chemical hoses and pump liners.

5.19 Polychloroprene (CR)

Neoprene is the generic name for polychloroprene rubber. It has been produced commercially since 1931 and had rapid and wide acceptance because it is much superior to natural rubber for heat and oil resistance. Heat resistance is far better than NR, BR or SBR. but less than EPDM. When heated in the absence of air, neoprene withstands degradation better than other elastomers which are normally considered more heat resistant, and retains its properties fifteen times longer than in the presence of air. Compression set at higher temperature is better than natural rubber and 100°C is typically the test temperature rather than 70°C. Abrasion resistance is not as good as natural rubber but generally better than most heat resistant and oil resistant rubbers. This is also true for tear strength and flex resistance.

The resilience of gum neoprene vulcanizates is little lower than natural rubber but it decreases with increased filler incorporation. Therefore, the resilience of most practical neoprene compounds is higher than that of natural rubber with comparable volume loading. Because of the presence of chlorine in the neoprene molecule, products made from neoprene resist combustion to a greater degree than products made from non-halogen bearing rubbers. This means neoprene can be compounded to meet the flammability requirements of the Mine Safety and Health Administration (MSHA) USA or similar requirements as might be stipulated by any other countries, conveyor belts flammability program and various other flammability tests without massive loadings of soft mineral fillers and special flame retardant plasticizers. Such loadings in non- halogen bearing rubbers lead to much poorer properties such as abrasion resistance and tear strength. While the oil resistance is not as good as some highly polar rubbers such as nitrile, neoprene compounds are generally considered moderate in oil resistance. Compounded with red lead, neoprene compounds are very water resistant. This leads to its use in oil well industries and processes where oily water and acidic fumes are encountered such as in fertilizer processing.

These same types of compounds are also more resistant to many acids at high temperatures than natural rubber can handle. Neoprene should not be used in parts which are bonded to metal for hydrochloric acid service because acid migration can cause failures. For hydrochloric acid service ebonite lined mild steel equipment is the correct selection. Ebonites form rubber hydrochloride film in contact with natural rubber and this film is the protective layer against corrosion.

Processing of neoprene is generally fairly good but compounds are relatively fast, curing at lower temperatures and therefore scorchy, and so care must be taken in selecting suitable compounding ingredients, mixing, calendering and extrusion processes to prevent premature vulcanization which is called scorching. Tack and adhesion in neoprene is generally quite good and, therefore, building composites with neoprene rubber such as expansion joints for pipelines is very practical and used in customized hand built hoses and belts. Good tack and green strength facilitate lining of vessels and pipes and intricate structures. With these properties neoprene is very commonly used for making adhesives and cements for bonding with metal and various other substrates. The adhesive system generally consists of two parts, the first part being a neoprene solution without accelerator and the second one with the accelerator such as isocyanates. These adhesives are designed for room temperature curing of the bond ,commonly known as cold bond system, which is adopted in site lining of large storage tanks situated in open areas such as in harbour terminals and ship and rail tankers.

The cost of neoprene is very high when compared to NR, BR, or SBR and even other heat resistant and ozone resistant rubbers such as EPDM. So when EPDM can be used for such conditions for ozone and heat and not flame resistance, it should be the preferred rubber in place of CR.

5.20 Nitrile Rubbers

Simple nitrile elastomers are copolymers of acrylonitrile (ACN) and butadiene monomer (NBR), the ratio ranging from 18/82 to 50/50. The basis for selection of a particular grade of nitrile rubber having a particular monomer ratio is usually governed by oil / solvent resistance as well as the low temperature performance required in the final vulcanizate. Higher ACN gives better oil resistance, but poorer low temperature properties. Using the same base compound formulation a 45% ACN polymer will give a compound with 0% swell in ASTM #3 oil after immersion for 70 hrs at 140°C while a 18% ACN polymer leads to 30% swell. The 45% ACN compound has a brittle point of –8°C while the 18% ACN compound is –58°C. As the ACN content increases, tensile strength and hardness increase while the resilience and compression set resistance decrease. A medium nitrile rubber can be a compromise for optimizing the properties while fabricating components in oil well application. Heat resistance of NBR is generally good and can be enhanced with special compounding techniques and by using polymers with built-in antioxidants. For ultimate heat resistance, a hydrogenated nitrile (HNBR) has been successfully used for seals in a smelter operation at 200°C handling very abrasive and corrosive fly ash. Resistance to impinging abrasion is very fair as resilience is generally low with normal ACN levels. Resilience to sliding abrasion is also fair but can be dramatically improved by using carboxylated nitrile rubber (XNBR). Flex resistance of NBR products is fair and can be improved further with special antioxidants. HNBR rubber compounds have outstanding flex resistance. Resistance to polar fluids decreases with increasing ACN levels and there are usually better choices for resistance to acids, bases and water than NBR. HNBR has much better resistance to oxidizing fluids and can be used in hot acids and bases. HNBR has been used in water service, under high pressures at up to 175°C. Ozone resistance, except for HNBR is generally poorer for NBR compounds but can be improved by blending with polyvinylchloride. This leads to uses in such applications as chemical hose covers, conveyor belts , fluid resistant special components such as gaskets, sheetings, etc., for chemical industries. NBR/PVC can also be blended with NR or SBR to give moderate oil resistance and abrasion resistance. The tack of the NR portion allows such blends to be used in lining of chemical process tanks and vessels pipes and hand lay-up products. The processing characteristics are good for all the nitrile rubbers, except for tack which has to be improved with suitable plasticizers. However this lack of tack limits their successful use in hand-lay up products. The cost of NBR is between CR and NR, and XNBR can be a little costlier. HNBR compounds are approximately ten times the cost of NBR which limits their use to products which absolutely require their unique properties.

5.21 Chlorosulphonated Polyethylene (CSM)

Chlorosulphonated polyethylene was first introduced by DuPont as Hypalon, a trade name in the year 1952. Chlorosulphonated polyethylene compounds have good heat and oxygen and ozone resistance, moderate oil resistance and excellent electrical properties, but their main features for use in the chemical process industries is their resistance to strong oxidizing chemicals.

Reaction tanks, pipings and pumps handling corrosive chemicals including dilute sulphuric acid at 60% to 70% concentration level are generally lined with hypalon compounds and hoses and tubes for such services are also made with this rubber. Good colorability required for the cable jacket manufacturing industry is an additional feature with this rubber along with its other good properties. CSM compounds can be used widely as geo membranes for lining reservoirs. They are installed in an uncured state for simple seaming at edges and repairs if necessary, and then the cure takes place slowly during subsequent ageing, giving an increase in toughness and durability. Processing of CSM is a little different from most rubbers in that CSM is more thermoplastic and softens more with heat. Compounds tend to become scorchy during processing. Tack is not very good and so hand lay-up products should be avoided or should be done with extra care with use of suitable solvents or adhesives. While manufacturing chemical hoses, neoprene cement is often used as a tie coat between layers and the built-up hose is machine wrapped with fabric before curing. Even for building up layers of hypalon sheets, a thin solution of neoprene adhesive is used between plies. The cost of CSM compounds is generally a little more than neoprene compounds.

5.22 Silicone Rubber

Silicone rubber has both excellent low temperature and high temperature properties. It can withstand temperatures up to 315°C and workable at –65°C. Poor performance with low tear strength and abrasion resistance limit their use in most applications. Liquid silicone compounds LTV which are room temperature vulcanizable are useful for small repairs and sealing application and have been used for poured-in-place gaskets.

Silicone rubbers are obviously not recommended for use in the temperature range where other less expensive rubbers are capable of serving (generally all rubbers' temperature rating being about –25°C to 125°C) unless some specific property of silicone rubbers other than the heat resistance is required. They are economically and outstandingly used at temperatures where other synthetic rubbers cannot serve. No other rubbers surpass the silicone rubber in the range of temperatures over which the useful rubber character is retained. This property of low sensitivity to temperature change coupled with good electrical properties has been a great factor in the commercial development of various applications.

The silicones are ideally suited for the construction of stationary or static seals for high temperature oil lines because of their cold flow at high temperatures. The packing seal is supported within a mechanical framework underneath a spring loading device so that the rubber is at all times under mechanical stress. Under these conditions it flows into the physical irregularities of the metal and effects an initial seal. Gaskets of silicone rubbers can withstand temperatures and in many cases solvents such as pyranol (molecular formula: $C_5H_6O_2$) and chlorinated hydrocarbons to which conventional rubbers are not resistant. Pyranol is polychlorinated biphenyl (PCB). Monsanto used the trademark Aroclor while GE used the trade name Pyranol to denote its version of Monsanto-produced PCBs. The Transformer Manufacturing Division of GE manufactured large and medium-sized AC and DC power transformers. Pyranol was used by GE beginning in 1932. PCBs were used in capacitors, transformers, hydraulic fluids, lubricants, carbonless copy paper, inks, pesticide extenders, sealants and flame retardants. However PCBs were banned in USA [9] because of health hazards, and use of silicone in this duty condition has become redundant. The properties of silicone rubbers that can be improved at times are their comparatively low tensile strength, tear strength and abrasion resistance and their relatively high compression set at very high temperatures. With respect to the later property it should be noted that the temperatures referred to are higher than the service temperature ratings of any other rubbers and consequently compression set at high temperatures is not a disadvantage in silicone rubber by comparison with any other rubber material, but it can be considered as a property which if improved by research and development work can be desirable. Reinforcement of the rubber with glass or asbestos cloth increases its resistance to compression set and its resistance to tearing. Since the silicone rubbers are odorless, tasteless and non-toxic they have found use in wire and glass cloth reinforced conveyor belts for food processing industries. The silicone rubbers have opened wide possibilities for the design engineers as shown by the illustrations given above.

5.23 Thiokol or Polysulphide Rubbers (T)

The most important uses of the Thiokol rubbers depend largely on their excellent resistance to oils, solvents and water and their impermeability to gases. These are used in gasoline hose, in oil loading hoses and as the hydrocarbon resistant bulletproof tanks for airplanes, fuel depots and boxcars adopted for the transportation of fuel oils, in protective coatings, etc. Asbestos impregnated with Thiokol is used as a flexible seal for floating roofs of gasoline storage tanks. Polysulphide rubbers also are available in powdered form for flame spraying. The most important application of flame-sprayed Thiokol is in coating rudders, struts (structural and pipe supports), and steel shafts fitted with bronze propellers for use in mine sweepers and other vessels. Corrosion caused by cavitation and electrolytic action between dissimilar metals in seawater is thus eliminated. Other uses of flame sprayed material include lining of salt water pipeline valves and low pressure condenser plates.

5.24 Polyurethane (AU or EU)

Most polyurethanes are different from other elastomers in that they are cast. Two components are mixed together. One component is a prepolymer which consists of two major chemical structures. One is an isocynate usually methylene bisphenyl diisocynate (MDI) or toluene diisocynate (TDI). The other is a polyol which is either a polyether (EU) or a polyester (AU) The other component is a curative which contains hydroxyl or amine groups. Urethanes have excellent physical properties including high tensile strength and tear strength, high resilience and excellent resistance to non-polar oils, fuels and ozone. Compared to other elastomers, polyurethanes tend to have their optimum properties at much higher hardness and modulus. This leads to higher load bearing capabilities and to withstand higher tip speeds in urethane lined pump impellers used in fertilizer and other process industries than softer elastomers. As a general guideline, esters are better for tensile strength, tear strength, sliding abrasion, oil resistance and heat resistance. MDI ethers are better for rebound and low temperature properties and impinging abrasion and hydrolysis resistance.

The limitations of polyurethanes are chiefly three. Owing to certain thermoplastic characteristics their upper temperature rating is high around 110°C. Polyurethanes are subject to hydrolysis in the presence of moisture at high temperature. At low temperatures most polyurethanes can withstand continuous contact with water for years. No other rubber can withstand dry steam for prolonged periods. In between these two extremes polyurethanes may or may not be suitable for use. The MDI ethers are much preferred for hydrolysis resistance. (Hydrolysis is a chemical reaction during which one or more water molecules are split into hydrogen and hydroxide ions. It is the process of reaction that is used to break down certain polymers. Such polymer degradation is usually characterized by either acid, e.g. concentrated sulphuric acid, or alkali, e.g., sodium hydroxide, attack often increasing their strength or pH. Hydrolysis is distinct from hydration, in which the hydrated molecule does not break into two new compounds.

Sometimes a polyurethane component used in the wrong duty condition will appear to be performing better than the same part made from a more water resistant elastomer such as natural rubber and then it will fail rapidly. Certain chemical environments (strong acids and bases and polar solvents such as ketones or esters) are also unsuitable for polyurethanes because of their polar nature.

Processing of polyurethanes is different from other elastomers in that most polyurethanes are cast into a mold. The mixing of the pre-polymer and curative can be done with specially designed machines in large shops or by hand in small shops or for small runs.

Polyurethane is also available in millable gum form which can be handled on the same conventional rubber processing equipment and cured in similar molds.

Lack of knowledge, poor technical advice from suppliers and consequently the wrong choice of grade or improper processing are the main causes of comparatively less use of millable gum polyurethanes in the rubber industry.

5.25 Fluoroelastomers (FKM)

Practical fluoroelastomers introduced in the 1950s provide extraordinary levels of resistance to chemicals, oils and heat. VITON made by DuPont is probably the name most familiar to the chemical processing industries, although other companies in the USA, Europe and Asia produce a wide variety of different fluoroelastomers. Few fluoroelastomer products are specifically designed for mineral processing, but some are used in hoses and pump liners of small sizes to handle aromatic solvents such as toluene and very strong acids and "O" rings, gaskets and seals to handle aggressive chemicals and solvents at extreme heat. Processing of this elastomer is difficult. Tack is very poor. High temperature post cures at about 250°C are very often required and as such fluoroelastomer is not used in lining application and due to its prohibitive cost, large tanks are not lined with this elastomer. They are more suitable for smaller components manufacture.

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6

Design Considerations for Fabrication of Equipment Suitable for Rubber Lining

Design and fabrication of tanks, vessels, piping and other equipment which are required to be protected with rubber lining against corrosion need special consideration in chemical plant construction. Certain features are to be incorporated in the design, and precautionary methods should be taken while fabricating the mild steel equipment to be suitable for rubber lining application. These are discussed below.

The equipment should be fabricated in such a way that the surfaces to be rubber lined are accessible to the eye and hand. Inaccessible points, for example, in the case of pipelines should be subdivided by providing extra flanges to facilitate rubber lining as shown in the figure 6.1. Pipe lengths should be kept to a minimum wherever possible.

The design of all vessels and equipment shall allow for adequate access and venting of fumes evaporated during usage of solvents for surface cleaning and adhesive coating thereafter.

In completely enclosed vessels, there must be at least one manhole of size not less than 18″ × 16″ if it is in rectangular shape. If the manhole is in circular shape, the diameter of the same should not be less than 18″ with an additional branch pipe fitting of 3″ diameter.

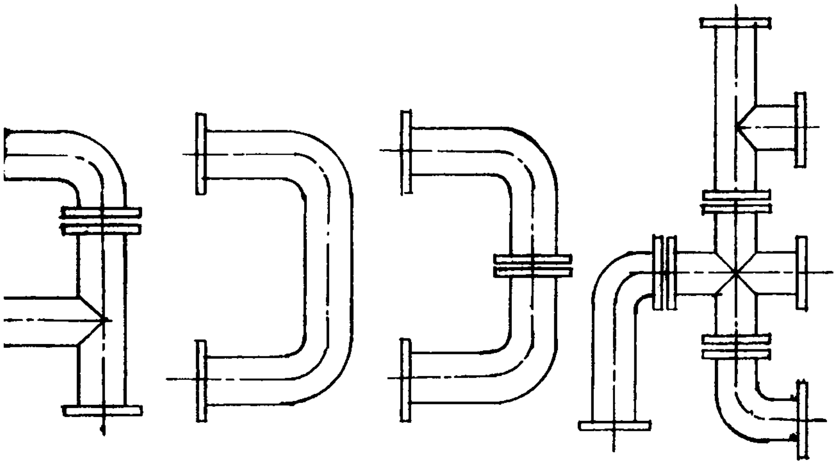


Figure 6.1 Subdivided pipelines with flanges.

Due allowances should be given for the thickness of the rubber lining while calculating the volume capacity of the tank or vessel and the clearances.

The surface to be rubber lined should be free from pitting and other metal imperfections. Sharp corners and contours should be subdivided wherever possible and finished to a suitable radius.

Any steam coil or immersion heater used for heating the contents of the vessel should be situated not less than 4″ away from the rubber lined surface to avoid local overheating. While heating by steam injection for curing, care should be taken to avoid direct impingement of steam onto the rubber surface.

While welding branch fittings in pipes and vessels, the weld projections and rubber lining projections should be outwards. Stitch welding from outside is preferred as shown in figure 6.2.

Threaded holes cannot be rubber lined and as such should be avoided in the design.

Screwed fittings should be avoided.

Laminated pipes and sheet metals are unsuitable for rubber lining.

Riveted and overlap joints are not recommended for rubber lining and should be avoided.

Flanges should have flat surfaces.

Dye penetrant test on the welded surfaces for any blowholes should be conducted before the equipment, pipes and fittings are subjected to hydraulic testing.

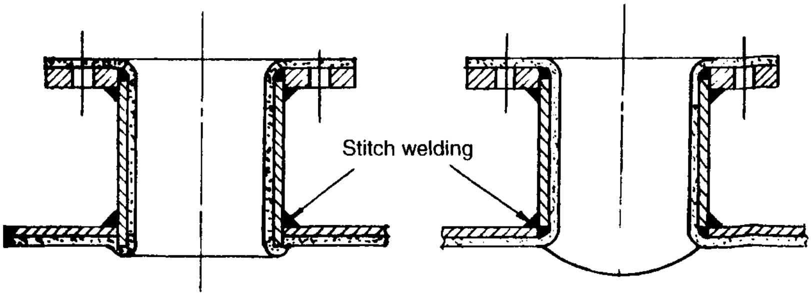


Figure 6.2 Outward rubber lining projection and stitch welding. Rubber lining is shown in dotted lines.

Pressure vessels and pipes should be subjected to hydraulic testing before rubber lining.

6.1 Mild Steel Vessels

Mild steel vessels should be fabricated and tested in accordance with recognized engineering standards of design and practice to meet the requirements of transportation and to endure mechanical and thermal strains while applying the protective rubber lining as well as the working load. If necessary, reinforcements should be provided on the unlined surface. The inner and outer edges of the equipment should be rounded off perfectly as shown in figure 6.3.

Only welded and seamless construction should be adopted. Butt welds in both butt joints and T joints should be made with more than one run of electrode or blowpipe. The weld should be ground smooth and flush. Welding should be done from the side to be rubber lined wherever possible, as shown in fig 6.4 A. Where

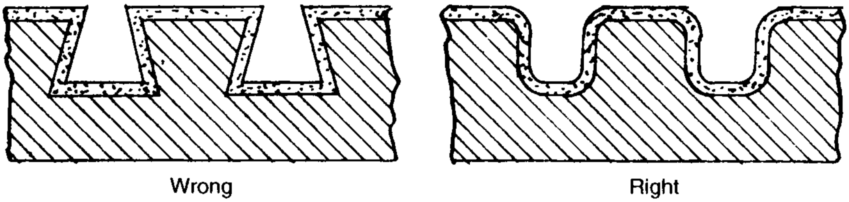


Figure 6.3 Rounded off edges. Rubber lining is shown in dotted lines.

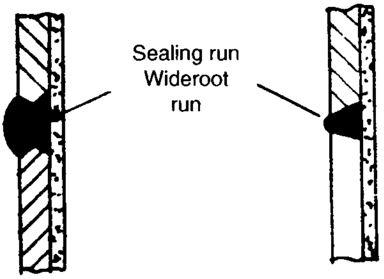


Figure 6.4 A Welding from rubber lined surface Rubber lining is shown in dotted lines. B Welding done away from the rubber lined surface.

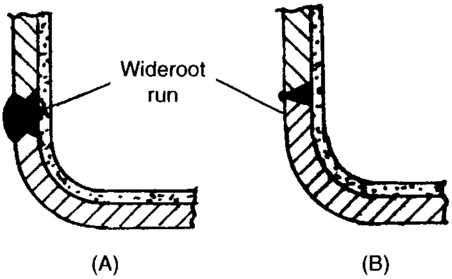


Figure 6.5 Corners without joints. Rubber lining on plain surface at corners is shown in dotted lines.

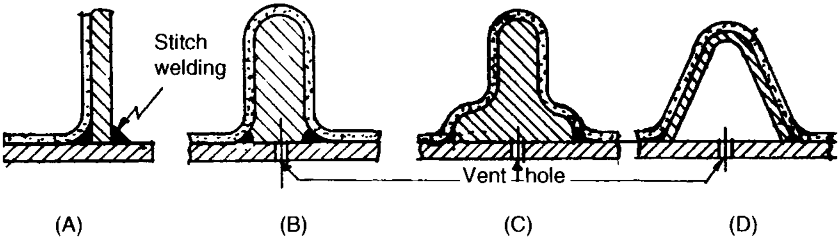


Figure 6.6 A shows welding without vent hole, B, C and D with vent holes.

it is not possible to weld from the side to be rubber lined, the root should be chipped out and a sealing run should be used as shown in figure 6.4 B.

Equipment with a flat bottom should be fabricated and finished as shown in figures 6.5 A and 6.5 B below, so that rubber lining at corners will be on plain surfaces instead of on the welded

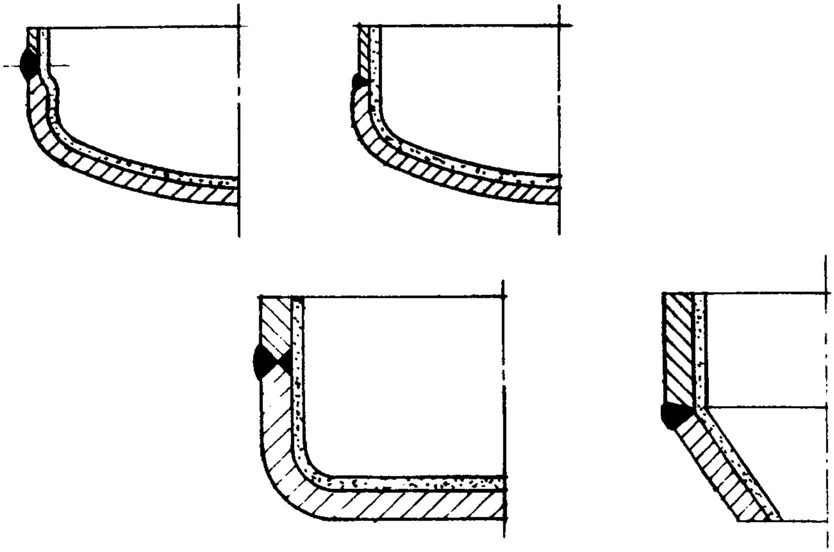


Figure 6.7 Dished ends, conical bottoms and flat bottoms.

surfaces, thus avoiding joints at the corners which are prone to be separated.

In cases where corner joints are unavoidable while constructing tanks, it is necessary to ensure that there are no air pockets, pits or surface irregularities at weld joints to avoid possibility of air trap between the rubber lining and the metal surface. For this, suitable vent holes are to be provided. A typical method of avoiding air being trapped in weld joints is shown in figures 6.6 A, B, C and D.

Adequate provision should be made in the design of mild steel tanks to withstand pressure vulcanization after rubber lining where the tank is intended to be pressure vulcanized.

If the tank is intended to be lined and vulcanized in the autoclave, the overall dimensions of the tank or its sections and branch pipes should suit the size of the autoclave.

In the case of centrifuges, stirring rods, fans, blowers and vibrating containers where often big centrifugal forces show up, they should be dynamically balanced immediately after fabrication and before rubber lining. Sometimes, balancing rubber pads are fixed on the equipment after lining to ensure that the same is dynamically balanced.

Dished ends, conical bottoms and flat bottoms of the tanks should be provided as shown in figure 6.7 above.

6.2 Pipes and Fittings

Sizes of pipes of diameter up to 6″ and below should be of seamless quality. Sizes above 6″ may be of ERW/seamless quality If ERW pipes and fittings are used, the weld seam should be ground flush with the parent metal to ensure a continuous smooth surface. Defects such as dents, delaminations, pitting, extrusion defects and other metal imperfections on the interior surface should be totally eliminated. Spiral welded pipes are not suited for lining. While bends and elbows are fabricated by bending, the concentricity at the bend position should be maintained correctly or otherwise lining will be likely to fail at that place. Flange position should be made as illustrated in figure 6.8 below. The side to be protected with lining should be continuous, and the edges at the junction should be removed and the surface should be ground smooth. On the surfaces where lining is not required the welding should be intermittent to avoid airlock.

In the case of centrifuges, stirring rods, fans or blowers, vibrating containers, etc., where big centrifugal forces often show up they should be dynamically balanced immediately after the fabrication and before rubber lining. In the case of soft metals like aluminium, it is recommended that the design should provide for maximum rigidity.

The recommended dimensions of pipes and fittings for satisfactory lining with ease of access are given below in tables 6.1 6.2, 6.3 and 6.4.

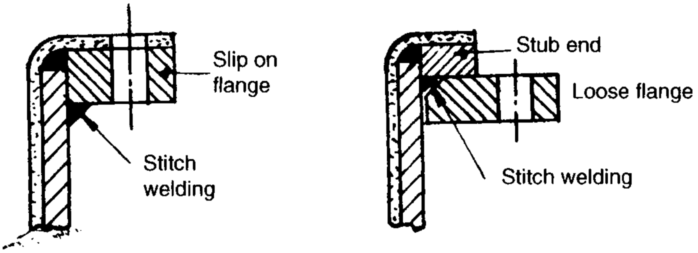
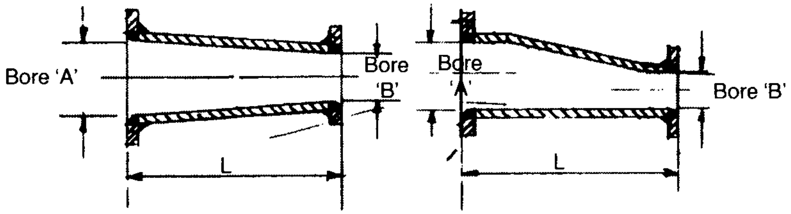


Figure 6.8 Flange position.

Table 6.1 Pipe Fittings



(A) Concentric (B) Eccentric

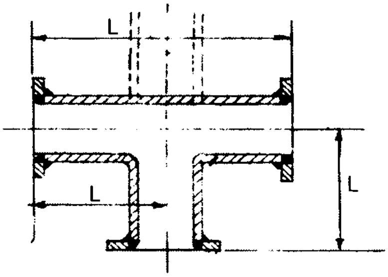
Dimensions of concentric and eccentric reducing pipes for satisfactory lining.

Nominal Bore (A) mm	Nominal Bore (B) mm	L mm
40	25	150
50	40	200
65	50	200
80	65	200
100	80	250
150	100	300
200	150	300
250	200	300
300	250	450
350	300	450
400	350	450
500	400	600

Table 6.2 Straight pipes

Nominal bore diameter (mm)	**Maximum length between flanges (mm)**
25	1000
40	2000
50	3000
65	4000
80	5000
100 and more	6000

Table 6.3 Tee pieces, crosses and branch pipes



Dimensions of Tee pieces, crosses, and branch pipes for satisfactory lining.

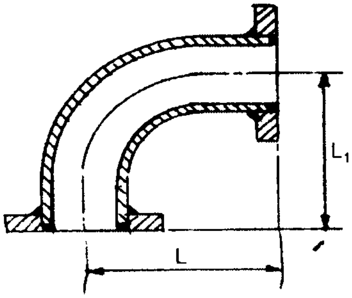
Nominal bore mm	L (max) mm	L_1 (max) mm
25	100	1000
40	120	2000
50	130	3000
65	140	4000
80	150	5000
100	180	6000
150	230	6000
200	280	6000
250	330	6000
300	380	6000
350	430	6000
400	480	6000
500	580	6000

6.3 Metal Defects Detrimental to Rubber Lining

Failure in rubber lining may occur due to the following defects in the fabricated metal:

- Blowholes in the welding.
- Improper grinding of weld seams at corners and sharp edges.
- Air inclusion during welding since proper vents are not provided.
- Lamination on the metal plates used for fabrication.
- Deeply pitted surface on the metal.

Table 6.4 Bends and elbows



Dimensions of bends and elbows for satisfactory lining.

Nominal bore mm	L (max) mm	L_1 (max) mm
25	100	100
40	120	120
50	150	150
55	170	170
80	200	1000
100	240	1500
150	350	1800
200	400	2000
250	520	2000
300	610	3000
350	610	3000
400	750	4000
500	950	4000

- See page of moisture into cracks and delaminations.
- Chemical deposits on the lining surface in the case of re-rubberlining of the equipment.

Blowholes and air inclusions are the flaws most difficult to detect during inspection of the equipment for rubber lining. The blowholes, cracks and holes on the surface could be detected by dye penetrant test (DP test) and also by radiography and ultrasonic methods. The laminations, sharp edges and weld seams, pitted surfaces and inaccessibility for lining work are visually inspected and rectified. Chemical deposits are best removed by solvent cleaning or steam sweating.

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7

Chemical Process Plants and Equipment

7.1 The Chemical Process

A chemical process is a combination of steps in which starting materials are converted into desired products using equipment and conditions that facilitate that conversion. We know that chemistry involves the use of chemical reactions to produce a desired product. Supposing we want to make a product "C" from chemicals "A" and "B" through a reaction it would be expressed in the following simplest manner.

$$A+B \rightarrow C$$

In the laboratory we may conduct this reaction by pouring chemical A into a test tube and B into another test tube. We may then heat each test tube in a laboratory burner to increase the temperature at which these two chemicals will react. The next step we follow may be to mix the two hot materials together so that they can react to produce the desired finished product C. Finally if other chemicals are present along with C which is the product mixture we need to separate C from the mixture by various methods such as

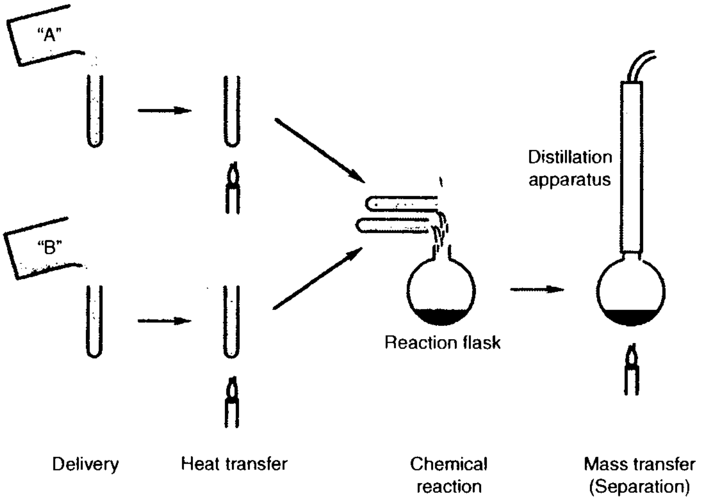


Figure 7.1 Schematic diagram of a laboratory process producing "C" from "A" and "B".

precipitation, evaporation, filtration, sedimentation, concentration, coagulation or selecting a suitable method from quite a number of other steps known to us.

In an industrial setting, a more efficient way to make chemical C rather than hiring a number of laboratory chemists with test tubes is to use an automated chemical process. We intend to do this to produce a larger quantity of the product C or to produce a smaller quantity of it with very high quality. Schematic diagrams of a laboratory as well as industrial processes are shown in figures 7.1 and 7.2 [1].

In the latter case the procedure corresponding to the laboratory process will be to pump chemical A from a tank through a pipeline containing a heat exchanger (which transfers heat from a hotter medium to a colder medium). A similar procedure is followed for B involving again a pump, pipeline, tank and heat exchanger.

These reactants A and B are thus brought together in a reactor with the required temperature, pressure and catalysts to speed up the reaction. It is important that the reactor is designed with a suitable material of construction in such a manner that chemicals A and B spend the required reaction time. The final step might be to send the product to a continuous distillation unit or to a settling tank or to any other device which may be called as a separator which would separate C away from other chemicals in the stream. The additional

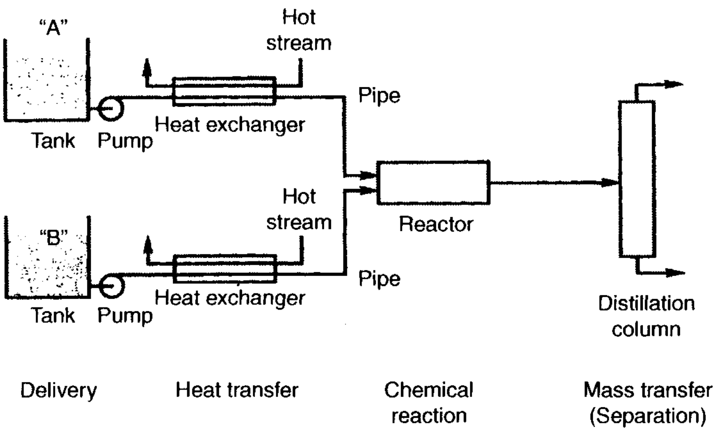


Figure 7.2 Schematic diagram of an industrial process for producing "C" from "A" and "B".

feature of an industrial process not found in the laboratory process consists of materials of construction of the equipment for protection against corrosion which is the result of almost all materials undergoing reactions and being exposed to atmosphere and severe corrosive environments in most process industries. This is all about chemical engineering sufficient enough for the understanding of a layman. But the fact that the chemical engineers are making important contributions to society in an extraordinarily wide range of fields that span from microchips to banana chips, thus making chemical engineering an exciting discipline, cannot be overlooked. The fact that the chemical engineer is handling versatile fields of industries to serve society is well illustrated in the figure 7.3.

The understanding of the design and construction of a chemical plant is fundamentally regarded as the essence of chemical engineering, and it is this area where a mechanical engineer is responsible for ensuring strength of plant and equipment structures and the rubber technologist is concerned with combating corrosion and erosion of the same. Throughout the process industries, there are many physical operations common to a number of individual industries and these may be regarded as unit operations. These operations involve solids and liquids and gases, most of which are corrosive. Several of the unit operations aim at achieving a separation of the components of a mixture. The problems of constructing a plant and equipment for a fermentation industry, perfume industry, petroleum industry

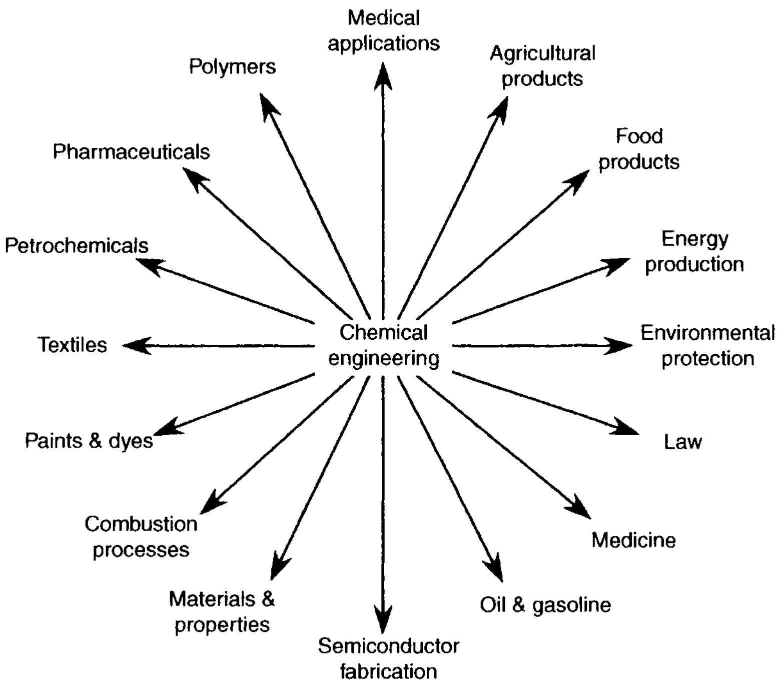


Figure 7.3 Areas of chemical engineering.

or other organic or inorganic chemicals industry are in principle the same, and it is mainly in the details of construction the difference will occur. The introduction and removal of the reactants in a reactor vessel may present difficult problems both in a batch scale process and a continuous scale process, especially if they contain corrosive or abrasive materials, and here is where a rubber technologist is more concerned about offering a material of construction to the plant and equipment. It is essential, therefore, that the rubber chemist is familiar with the basic details of the plant and equipment.

Some of the details of the process plant and equipment are discussed below.

7.2 Flue Gas Desulphurization Systems (FGD)

In flue gas desulphurization systems, equipment such as absorber towers, demister supports, gas outlets, recycle and process pipings, process tanks, and agitators are highly exposed to corrosive and abrasive environments. Chlorobutyl rubber of 60 Shore A durometer is used for the FGD absorber and associated demister internals and other component pipings. For agitators rake arms gypsum dewatering, natural rubber of 60 Shore A is suitable. FGD absorber case histories confirm that the chlorobutyl linings give trouble free service when correctly applied and cured [2]. Chlorobutyl linings offer excellent chemical, heat, weather and ozone resistance compared to natural rubber.

However, the 60 durometer natural rubber specifically compounded for the FGD rubber absorption pipe has double the abrasion resistance compared to the chlorobutyl linings used in FGD absorbers. In selecting a rubber lining for pipe, either for recycled slurry, reagent feed, gypsum dewatering, or filtrate systems, one must take into account the volume flow, percentage of solids and particle size in order to make the proper choice. Laboratory tests comparing various durometer materials showed vast differences in water absorption. A 40 durometer natural rubber gains five times the amount absorbed by a 60 durometer lining. Where abrasion is considered severe, 60 durometer natural rubber is the proper selection. When moderate to light abrasion is encountered, 60 durometer chlorobutyl lining may also be utilized.

In many FGD pipe applications, 40 durometer pure gum rubber gives only 3–7 years of service, whereas a 60 durometer natural rubber gives 7–10 years of life. Since most FGD scrubber piping encounters very light abrasion, installing chlorobutyl is expected to last in excess of 15 years. Chlorobutyl is better for the absorber and the demister supporters as the performance lining.

7.3 Water and Waste Water Treatment Equipment

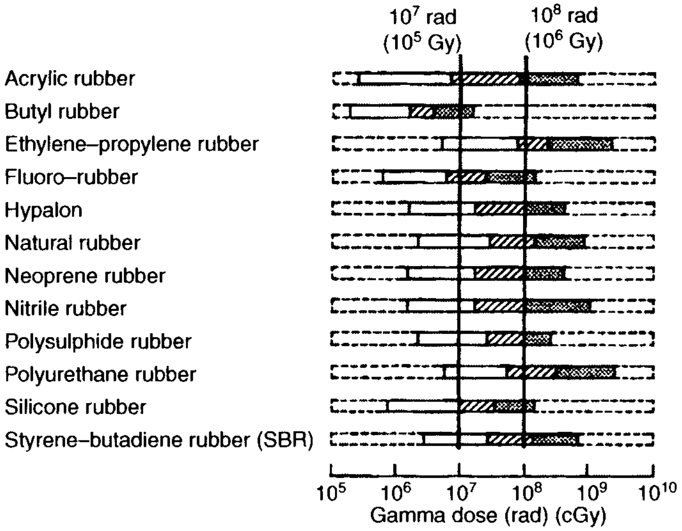
The water treatment units are: pressure filters, ion exchange and condensate polishers.

Suitable rubber linings for water and wastewater treatments are:

Natural Rubber 60 Shore A durometer. Natural rubber is designed for low water absorption in clarifiers and condensate polishers. Light coloured natural rubber offers ultrapure water protection. It has the same excellent acid and water resistance as the black rubber lining with the added features of being white and conformimg food grade. Both 80 durometer or 90 durometer linings offer excellent water and chemical resistance and are food grade compounds for ion exchange units and filters. The lower durometer rubber has greater impact resistance.

7.4 Nuclear Power Water Treatment Plant

The need to maintain elasticity of rubber is of paramount importance under any serious and severe environmental conditions. The most stable rubbers in radiation environments are polyurethanes and phenyl silaxanes which are usable at well above 10^8 rads (10^6 Gy). Butyl rubber liquefies and neoprene evolves hydrochloric acid at similar dose levels. Most polyurethane rubber foams can be used at a dose level of 10^9 rads (10^7Gy) in vacuum at temperature levels of between −85°C to +250°C. Silicone and polysulphide sealants are probably less tolerant to ionizing radiation in a nuclear plant where chemical processes are being carried out. A schematic graphical representation of the tolerance of rubbers to ionizing radiation in nuclear plant is shown below in figure 7.4.



Condition number	0	1	2	3	4
Damage condition	Undetectable	Incipient to mind	Mild to moderate	Moderate to severe	Destruction
Utility	Full use	Nearly always usable	Often satisfactory	Limited use	Not usable

Figure 7.4 Tolerance of elastomers to ionizing radiation.

7.5 Radiation Units

The Roentgen unit is the amount of energy deposition which creates air ions to the level of 2.58×10^{-4} coulombs per kilogram. This corresponds to the deposition of energy in air at the rate of 87 ergs per gram. The rad and gray (Gy) are universal units of energy deposition. A rad has been absorbed by a sample when 100 ergs per gram and a gray when one joule per kilogram has been deposited. One rad thus equals 10^{-2} gray or one centigray (cGy) [3].

The damage conditions of each rubber give clear information on the various rubbers exposed to ionizing radiation in the nuclear industry. The components in the nuclear equipment are gas flue outlets, recycle and process pipings, process tanks, and rake arms and agitators.

Nuclear facilities require sulfites to be at absolute minimum levels. In order to maintain these low levels when using semi-hard rubber linings in demineralizing water treatment units, the lining must be pressure cured, either in an autoclave or by using the vessel as its own autoclave. Only high steam pressure curing will cross link and combine the sulfur in semi-hard rubber linings. On the original vessel, this is not difficult because linings can be internally steam cured. Normal practice is that they be cured 12 hours at 260°F.

With older vessels requiring repairs, one has to make a judgment as to how to repair the vessel. Basically, there are two options for repair. One is to use a chemically curable lining that is appropriate to match the lining in the vessel. Chemical cure linings may have high leechable sulfite levels, even when cured with steam. Therefore, chemical cure linings are only considered acceptable on minor repairs.

The other option is to use the original semi-hard lining to repair with an internal steam pressure cure. However, one runs the risk of damaging the original lining when making a partial repair. Though the linings listed above will exhaust steam, the threshold level of leechable sulfites is not acceptable to the nuclear plants. Therefore, if one has a large area of repair, the safe practice will be to strip and re-line the entire vessel with a pressure cured lining.

7.6 Phosphoric Acid Equipment

Major equipment components in phosphoric acid plants are phosphoric acid evaporators, barometric condensers, storage tanks and rail cars, pipes and fittings and pumps, units in di-ammonium phosphate plants and scrubbers. The high performance compounds for the phosphoric acid plants are based on chlorobutyl, and semi-hard-soft natural lining for evaporators, condensers and storage tanks. A 65 durometer semi-hard neoprene rubber can be suitable for scrubber applications and di-ammonium phosphate (DAP) units.

Natural rubber, three-ply lining constructions known as triflex lining have been used through the years with considerable maintenance. To minimize maintenance and to enhance the linings for chemical resistance, chlorobutyl and neoprene have become the industry's preferred elastomeric linings. The primary reasons for selecting these linings are due to their excellent chemical and heat resistance and a higher tolerance to many of the additives and flocculants used in phosphoric acid production, storage, and transportation. They also offer flexibility being homogeneous linings and eliminating cracking on bolted flange connections. The three-ply construction known as triflex lining is designed specifically for hydrofluorosilicic acid units. This three-ply construction offers the center hard core rubber for enhanced moisture and chemical resistance. The top surface being chlorobutyl offers excellent benefits, such as chemical, heat, ozone and weather resistance.

7.7 Hydrochloric Acid Handling Equipment

Hydrochloric acid (hydrogen chloride), once called muriatic acid, is a strong, highly corrosive acid. The commercial "concentrated" or fuming acid contains 38% hydrogen chloride. U. S. P. grades range from 28% to 38%, with 37% HCl being most common. Highly corrosive environments are encountered in various HCl acid applications.

For storage tanks, tank trailers and tank cars, natural rubber lining on steel has predominantly been used for hydrochloric acid containment. The acid reacts with natural rubber hydrocarbon to chlorinate the surface, making an impermeable membrane. In concentrated hydrochloric acid, it only takes approximately three months for natural rubber crust formations to be in the range of 1/64 (.016") thickness in depth. This crusting effect makes natural rubber an excellent lining for HCl service. It is also the destructive mechanism of the lining in later years. As surface stress cracks develop the acid penetrates the rubber, forming a new surface crust. The cycle continues until complete lining failure eventually occurs. Lining service performance ranges from 7 to 24+ years depending on lining hardness selection, environmental conditions and vessel stresses. Through the years, service history has demonstrated that a pure gum natural rubber gives the longest lining life for concentrated HCl. Generally, the lower the durometer, the longer it remains flexible. For example, a 40/45 durometer natural rubber will reach 75/80 surface durometer after three months, a 30/35 durometer takes much longer to reach 75/80 and thus nearly doubles the long-term lining life. It is that extra hardness that impedes the rubber's ability to resist flex stresses as found in over-the-road trailers or rail cars. Contrary to pure gum recommendation for concentrated HCl, a 60 durometer natural rubber, is recommended for dilute (5–10%) HCl. In dilute acid service, the compounded natural rubber has less water absorption than gum rubber. Laboratory tests in some of the rubber lining vendors show 6–8% less water absorption for compounded 60 durometer lining as compared to a pure gum.

7.8 Sodium Hypochlorite and Other Bleach Equipment

Today, numerous manufacturing companies design and supply comprehensive lines of water treatment and fluid processing equipment for industrial water purification. Numerous rubber compounds have been designed to handle bleach and other chemicals over the years to give high performance linings for sodium hypochlorite and other bleaches. Bleach resistant lining for bleach service can be made from a chlorobutyl rubber with heat, weather, chemical and oxidation resistance. A butyl rubber tie gum is used for easy installation. A 50 durometer chlorobutyl is also ideal for process and storage units. Chlorobutyl has excellent oxidation, heat, chemical and water resistance. Chlorobutyl lining with a natural rubber tie gum is also a suitable combination for this service. A black chlorobutyl rubber construction is suitable for wet chlorine and sodium hypochlorite (under 10%) make-up vessels. In sodium hypochlorite make-up units, a 60 Shore A durometer, chlorobutyl rubber is specially compounded for oxidation and chemical resistance, while the hard 90 durometer center core rubber resists chlorine permeation.

A 60 durometer EPDM rubber for a pure bleach will not produce black speck contamination. It has the same excellent bleach and water resistance with the added feature of having food grade FDA compliance. All linings are to be designed for minimal shrinkage in cure and should have good thermal flexibility.

7.9 Gold Ore Processing Equipment

The gold ore processing equipment components are ore grinding circuit, pre oxidation and feed piping lines, flash vessel discharge, carbon regeneration units, thickener units, neutralization tanks and effluent disposal system. Suitable performance lining constructions for gold processing are based on:

1. 60 durometer natural rubber, for moderate abrasive feed piping for sliding abrasion, weather and chemical resistant neutralization and thickener tanks.
2. 70 durometer natural rubber lining for severe abrasion and high solid processing, for high cut, tear and abrasion resistance such as in ore breakdown, and tailing thickener operations.
3. 60 durometer chlorobutyl lining for leaching, neutralization, cyanide processes and carbon washing with excellent chemical, weather, heat and oxidation resistance and is used for leaching tank and carbon acid washing equipment.
4. 70 durometer neoprene lining for high heat and abrasion conditions. May also be used in areas requiring a moderate oil resistance.

Selection of the correct lining for a particular processing area is complex and involves a clear understanding of the processes since each area has distinct solution, corrosion and slurry characteristics. In general, erosion protection is one of the primary areas of concern and the abrasion severity often determines the lining selected in the ore beneficiation industry. The chemical media being handled by elastomer tank linings are increasing in number and diversity. To assist in the selection of the proper lining for various chemicals, chemical resistance charts have been provided by many suppliers of raw materials. They are only guides and should not be used otherwise. Since there are many important considerations in the selection of the appropriate lining as discussed in these chapters, it is advisable to consult the user engineers and the rubber technologists for selection of suitable lining constructions.

General process equipment common to most process industries has common features; a few equipment descriptions are detailed below.

7.10 Equipment for Evaporation

The rapid development of new products and process technologies in the chemical engineering sector involved many liquids with a wide range of physically and chemically reactive characteristics, all of which require concentration by evaporation. The type of equipment used depends largely on the method of applying heat to the liquor and the method of agitation. In the process of heating and agitation, the liquor becomes viscous, restricting flow. During evaporation, scales are formed and deposited on the surface of the equipment. The equipment, therefore, is protected by a suitable rubber lining which, in addition to being resistant to the corrosive nature of the liquor, has to fight against the wear due to scale formation and deposition during agitation. A diagram of an evaporator is shown in figure 7.5 below.

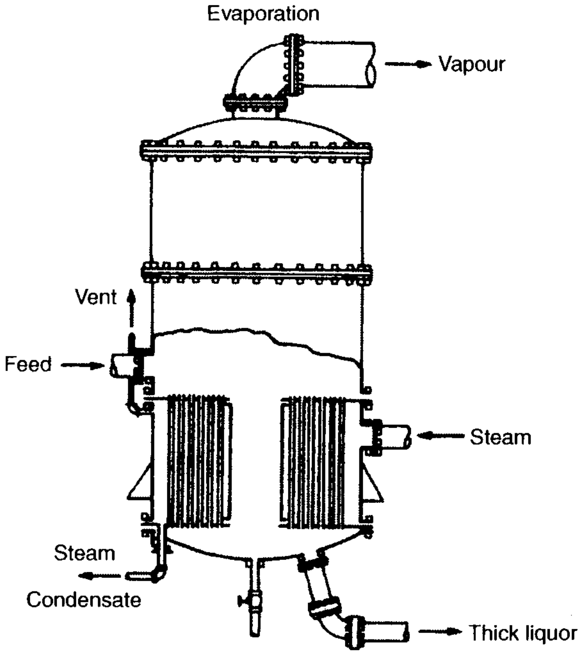


Figure 7.5 An evaporator - the vapour phase and the liquid phase will have different lining.

7.11 Crystallizer

Crystallizers are among the earliest equipment in the process industries and the process of crystallization is used to produce vast quantities of materials such as sodium chloride, sodium and aluminium sulphates which all have production rates of millions of tons per year world wide. Crystals are grown from the liquid phase - either a solution or a melt - and also from the vapour phase. A degree of supersaturation is essential in all cases for crystal formation and growth to take place. Some solutes are readily deposited from a cooled solution whereas some others crystallize only after removal of solvent. The addition of a substance to a system in order to alter the equilibrium conditions is often used in a precipitation process where supersaturation is achieved sometimes by chemical reaction between two or more substances and one of the reaction products is precipitated. In a crystallizer, therefore, one expects a physical and chemical reaction to take place under varying conditions of pressures and temperatures with agitating forces playing, all resulting in equipment wear and corrosion. Therefore it is necessary to develop different kinds of rubber materials suitable for the gaseous as well as the liquid phases.

7.12 Dryers

Dryers are equipment used for drying of the materials which are often the final operation in a manufacturing process to be carried out immediately prior to packaging and dispatch. Drying refers to the final removal of water or another solute and the operation often follows evaporation, filtration or crystallization. Drying is an essential part of the manufacturing processes and is carried out to achieve a quality product. The drying equipment has necessarily to be rubber lined against corrosion.

7.13 Cyclone Separators

These are used for removal of suspended dust particles from gases. The rate of settling of suspended particles in a gas stream may be greatly increased if centrifugal rather than gravitational forces are

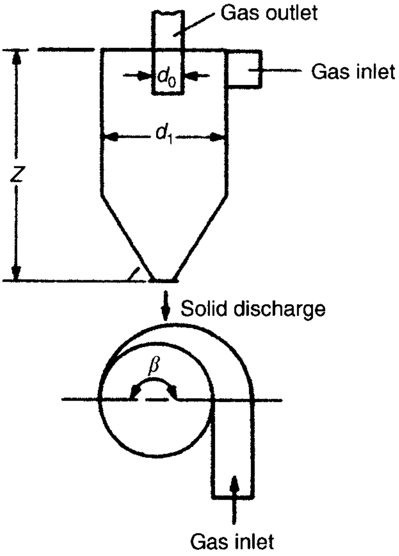


Figure 7.6 Schematic of a cyclone separator.

employed. In the cyclone separators shown in figure 7.6 the gas is introduced tangentially into the cylindrical vessel at a velocity of about 30 m/s and the clear gas is taken off through a central outlet at the top.

The solids are thrown outwards against the wall of the vessel and then move away from the gas inlet and are collected in the conical base of the equipment. This separation process is very effective unless the gas contains a large proportion of solid particles less than 10 μ in diameter and is equally effective when used with dust or mist-laden gases. The cyclone separators are obviously rubber lined to withstand wear at the velocity of gas and corrosion and are the most commonly used general purpose separator in the chemical process industry.

7.14 Thickeners

Thickener is the industrial unit in which the concentration of a suspension is increased by sedimentation in a solid-liquid system with the formation of a clear liquid. In many cases the concentration

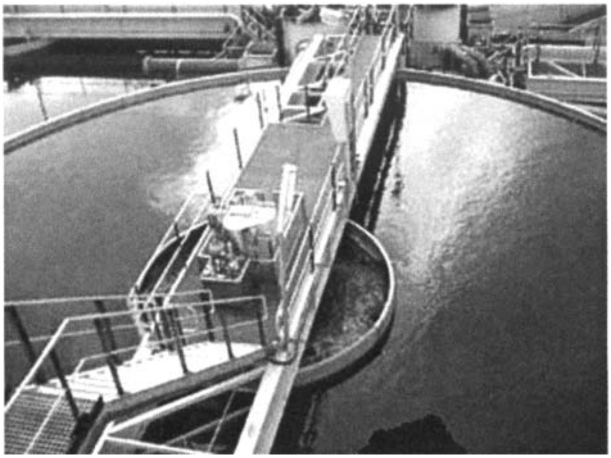


Figure 7.7 A Large thickener rubber lined and installed outdoor in the copper belt, Zambia.

of suspension is high and as such hindered settling takes place. Thickeners may operate as batch or continuous units and consist of tanks from which the clear liquid is taken off at the top and the thickened liquor at the bottom. Thickeners may vary from a few meters diameter to several hundred meters in diameter. A large thickener rubber lined by Bayers, Germany is shown above in figure 7.7. The total area of rubber lining of the thickener and its ancillary equipment is more than 10000 sq meters; it is installed in a Zambian copper belt.

Small thickeners are sometimes made of wooden construction as well as rubber lined steel. Very large thickeners are constructed with concrete and rubber lined. The components of such thickeners consist of stirrers, rake arms and tanks. The speed of rotation of such thickeners may be around 0.1 rpm.

7.15 Perforated Plates

A perforated plate is industrial equipment having numerous practical uses. Its construction is simple and complex at the same time. Metal plate was first perforated or punched back in the 1870s in Carbondale, Pennsylvania by an inventor and entrepreneur by the name of Eli Hendrick. He conceived the idea to punch multiple holes simultaneously in the raw metal plate as a means of speeding production. This idea of punching or perforating the plate revolutionized the production of perforated metal equipment.

Perforated plate is distinguished from a perforated sheet by the thickness of the material, to resist flexibility when the material is heavy. Plate can be perforated using a standard punching process, that is, a punch and die, in material up to 1 inch thickness. Depending on the metal being used, plate of this thickness or larger can also be perforated using a laser, a cutting torch, or a plasma torch or a high speed drilling device.

One of the most popular patterns for standard perforated plate would be a staggered perforation of round holes. This pattern is popular for a few reasons. It provides strength and a large open area which is ideal for sifting and separating particles of different sizes. The round hole on staggered pattern is also aesthetically pleasing to the eye which, of course would only matter in an application where the plate would be visible. Other patterns include a straight layout where the holes are in alignment both vertically and horizontally on the plate. Both the staggered and straight patterns can feature a variety of different hole shapes and sizes. Shapes include the standard square and rectangle as well as a hex shape, oval, and slot. Custom hole shapes can also be produced for various reasons through the use to a specially designed tool.

Although mild steel is one of the most popular choices for perforating, stainless and aluminium are also used. A rubber lined perforated plate is used in the chemical industry. The strength and durability of these perforated plate products make them ideal for use in many harsh industrial environments. A fine example is the mining industry where coal, stone, and other matter need to be separated or screened based on size. These shakers, as they are sometimes called, are good examples of the harsh, abrasive environment that a perforated plate may be subjected to. Perforated plate can provide solutions to a wide variety of complex and simple scenarios. Rubber lining of a perforated plate is a highly skilled job involving many joints which cannot be avoided. See figures 7.8 and 7.9 below of a rubber lined perforated plate.

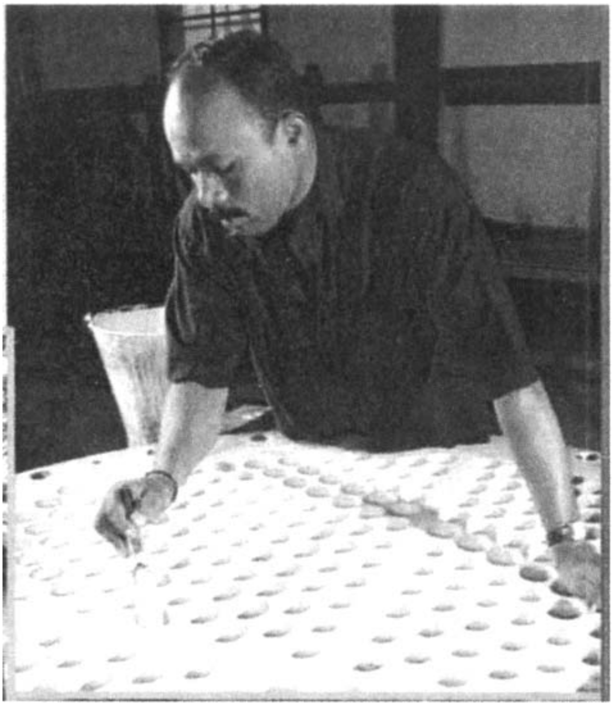


Figure 7.8 Adhesive coating being given on a perforated plate.

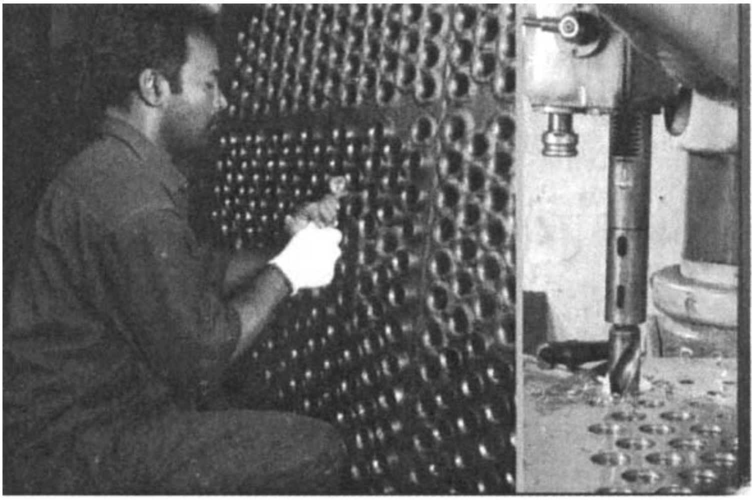


Figure 7.9 Rubber lining being done on a perforated plate- Insert- Holes are being punched in a metal plate by a drilling machine.

7.16 Industry Equipment and Components

7.16.1 Chlor-Alkali Industry

Washing compartments
Inlet elements
Mercury separators
Junction elements
Side channels
Cell covers (flexible and rigid)
Cell troughs
Pipes and fittings
Chlorine separators
Chlorine mixers
Hypo towers
Chlorine drying tower
Scrubber blowers
Evaporators
Decomposers
Dip pipes (fully rubber lined)

7.16.2 Rayon and Pulp Industry

Vapour heads
Mother liquor tanks
Storage tanks
Strainer boxes
Spin bath filters
Crystalizers
Zinc dissolving tanks
Degassifiers
Condensers
Separators
Evaporators
Slurry tanks
Hypo solution tanks

7.16.3 Fertilizer Industry

Crystallizer ducts
Return acid tanks
Conveyor drums and pullies

Vacuum washer vessels
Condensers
Filtrate tanks
Phosphoric acid storage and attack tanks
Agitators
Scrubbers

7.16.4 Mining Industry

Chutes
Hoppers
Slurry pipes
Coal handling system
Launders
Bolt-in rubber wear plates
Digesters
Clarifiers
Thickeners

7.16.5 Water Treatment Plant

Anion and Cation tanks
Degasser tanks
Pressure vessels
Saturators

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8

Processibility and Vulcanization Tests

8.1 Critical Properties of Rubber

The two critical properties of rubber and rubber compounds are their processibility and vulcanization. These characteristics are vitally important for the successful operation of all other steps of the manufacturing processes for the attainment of a final good quality and usable product. Hence it is necessary to measure these characteristics by conducting process tests and vulcanization tests. The mixed compound is subjected to application of force and since it is predominantly plastic, it will take the shape imposed upon it. This shape forming process can be accomplished by squeezing it between calender rolls, pushing it through a die having the desired profile in the extruder or by confining it under pressure in a mould cavity of required shape and size. This procedure is called processing of rubber and its measure is termed as processibility.

The plastic flow of compounded stock of rubber is dependent upon the temperature, force and the rate of force. Obviously these three variables are significant in measuring the processibility of rubber or its compound. After forming the stock to the desired shape, the compounds need to be converted into a strong elastic material. This is accomplished by the vulcanization process. The basis for vulcanization is chemical bonding or cross linking achieved by the use of sulphur and accelerators under elevated pressures and temperatures. During vulcanization the compound changes from an essentially plastic state to predominantly elastic state. At this state its inherent resistance to deformation increases. At the end of the vulcanization process the rubber is in its final form, the finished product. The tests of vulcanization measure the performance of the rubber compound during the curing process. In the measure of vulcanization the following terms need to be understood since they signify the various characteristics of the compound during the vulcanization process.

8.2 Scorch

Scorch is the premature vulcanization at an undesirable stage of processing where the compound becomes partly vulcanized. It reduces the plastic flow of the compound preventing further processing. Scorching is the result of both the temperature attained during processing and the amount of time the compound is exposed at higher temperatures. This period of time before vulcanization starts is generally referred to as scorch time. Since scorching ruins the stock, it is important that vulcanization does not start until processing is complete.

8.3 Rate of Cure

The rate of cure is the rate at which the cross linking and development of stiffness of the compound occurs after the scorch point. As the compound is heated past the scorch point, the properties of the stock change from a soft plastic to a tough elastic material. The rate of cure is an important parameter of vulcanization, since it, in part, determines the time the compound must be cured which is known as the cure time.

8.4 State of Cure

The state of cure is a term used to indicate the development of a property of the rubber as vulcanization progresses. As the cross linking and vulcanization proceeds the modulus of the compound increases to various states of cure. Technically speaking, the most important state of cure is the so-called optimum cure. Since all the properties imparted by vulcanization do not occur at the same level of cure, the state for obtaining a particular property may not be the best for other properties.

8.5 Cure Time

Cure time is the time required for vulcanization of the rubber compound to reach the desired state of cure for the desired property.

8.6 Over Cure

A cure which is longer than optimum is over cure. Over cures may be of two types. In one type the rubber continues to harden, the modulus rises and tensile strength and elongation fall. In certain cases, including most natural rubber compounds, reversion occurs with over cure leading to decrease in tensile strength and modulus.

8.7 Processibility

Processibility is dependent on the viscosity or plastic flow of the rubber compound,i.e., resistance to flow. Plasticity or viscosity determines the energy requirement of the rubber during milling, calendering or extrusion while the time to the onset of curing, i.e., scorch time, indicates the amount of heat history which can be tolerated before the rubber is converted from the plastic to the elastic state at which time processing becomes virtually impossible.

8.8 Plasticity

The rate at which the rubber compound is deformed has a significant effect on its apparent plasticity. The various processes such as mixing or milling, extrusion, calendering and moulding involve different levels of shear deformation and, therefore, can be expected to affect each stock differently. Thus the resistance to flow of two different compounds, even if they have the same flow characteristics and behave similarly and identically in the compression moulding process, would exhibit different flow behaviour under different deformation conditions that prevail in an extruder or calender. Therefore, tests which have been designed to ascertain the processing characteristics of a particular stock should ideally expose the test samples to deformation rates identical of those encountered in the actual process step. The tests, therefore, should be simulated tests representing the actual process conditions in an extruder or calender or any other processing steps.

8.9 Plasticity Tests

Plasticity test determines the deformation or flow of a rubber compound having little elastic recovery. It should be remembered that elasticity is present even in an un-vulcanized rubber and the energy will be stored in the compound during deformation and then released when the force is removed. Rubber before vulcanization is in between a plastic and an elastic state; when warmed up it becomes more plastic and less elastic. From commercial points of view, the plasticity tests are of little significance, but are important because their results assist in determining the processibility of the material and are used frequently for process control purposes.

8.10 Plasticity and Viscosity Test Methods

In general there are three accepted test methods for measurement of plasticity. One is the parallel plate type such as William's Plastometer, in which a rubber pellet of standard dimensions is squeezed between plates by applying a known force and measuring the deformation after a given length of time at a prescribed temperature. The second one involves extruding or mixing devices in which a quantity of rubber material is extruded through a small orifice or masticated in a small mixing chamber. These devices have the advantages that they closely simulate the conditions present

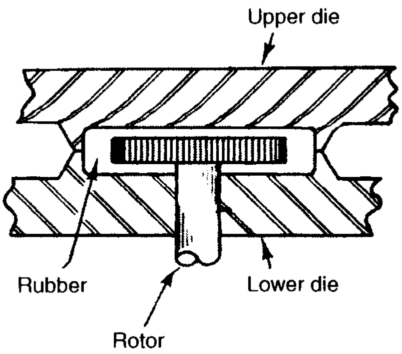


Figure 8.1 Mooney Chamber and rotor.

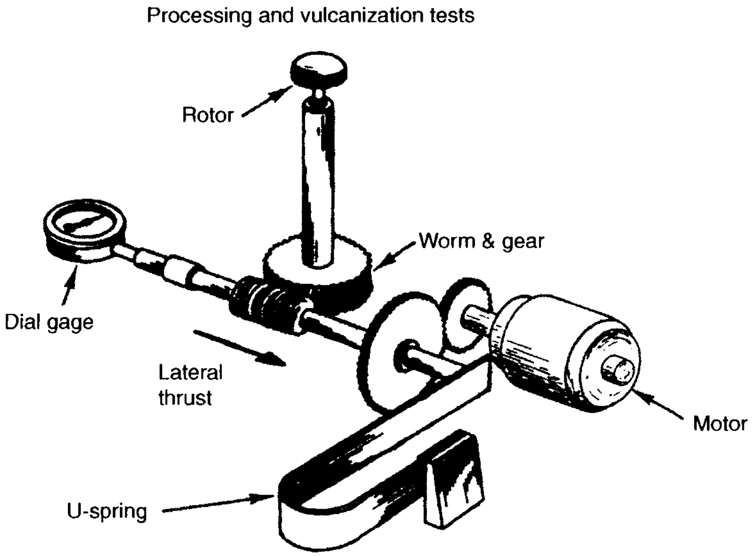


Figure 8.2 Mooney torque measuring system.

in the extruder or mixing mill in the actual factory environment. The last and the most widely used method is the rotating disc viscometer in which a knurled rotor is rotated in a mass of rubber contained in a mould chamber under pressure, and the torque required to rotate the rotor which can be either large or small is measured. Figures 8.1 and 8.2 depict the mooney chamber and the torque system.

8.11 Residual Scorch

Scorch may occur during the processing of the rubber compound due to the accumulated effects of heat and time. It is therefore obvious that the time for a given compound to scorch will slowly decrease as the compound moves through each stage in the process including the storage time of the in-process stock. Thus samples taken from the same batch at different stages in the process will have progressively shorter scorch time. The scorch time of a batch at a particular point in the process is called the residual scorch time. The effect of heat history on decreasing the scorch time of a compound can be studied on various samples taken from different stages of the process using the mooney rotating disc viscometer. See figure 8.3.

Any good factory stock should have a scorch time slightly longer than the equivalent of the maximum heat history it may accumulate during processing. If all the scorch time is depleted during processing it will be no longer processible and has to be scrapped.

The scorch behaviour of compounds is generally studied with the help of a mooney viscometer. The test is usually conducted at temperatures encountered during processing of the rubber stock. Typically this is in the temperature range of 250°F to 275°F. From a chart of mooney units vs test time, the time required for the

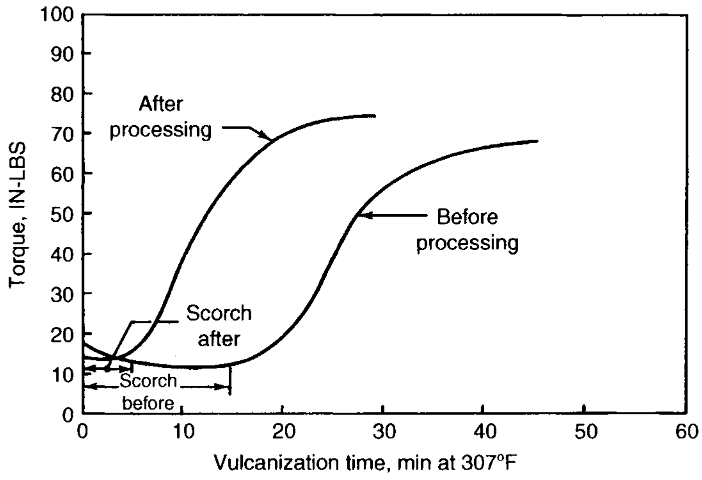


Figure 8.3 Effect of heat history on scorch time.

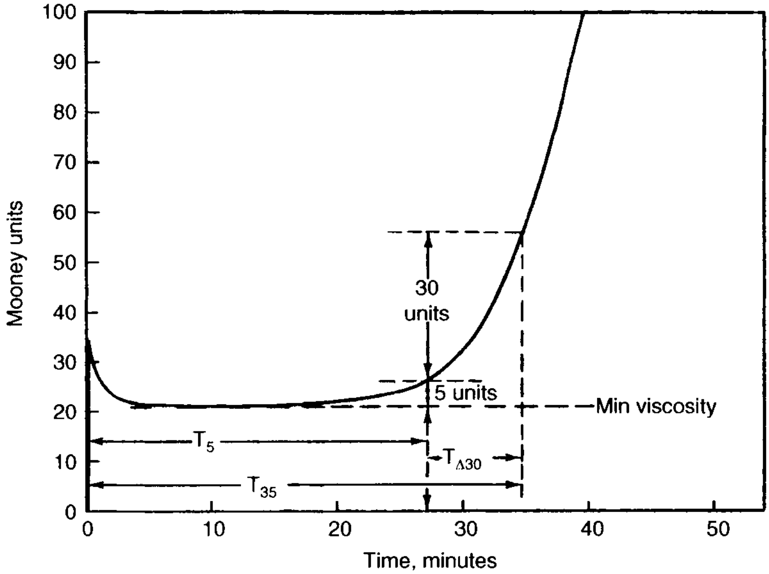


Figure 8.4 Mooney scorch curve.

compound to scorch (i.e., for vulcanization to start) can be easily determined noting when the cure curve turns upward as shown in figure 8.4.

The most common method of measurement is to run the compound in the mooney viscometer until the viscosity shows a 5 point rise above the minimum. The viscosity of the compounded rubber at the processing temperatures can also be obtained from the minimum of the curve. The values normally taken from the cure curve are:

MV = Minimum viscosity
T5 = Time to scorch at MV + 5 units
T35 = Time to cure at MV + 35 units
ΔTL = Cure index = T35 − T5

8.12 Vulcanization Studies

After the compound has been compounded by the addition of the appropriate curing agents, processed and formed, it is then vulcanized. The vulcanization process occurs in three stages: 1) an

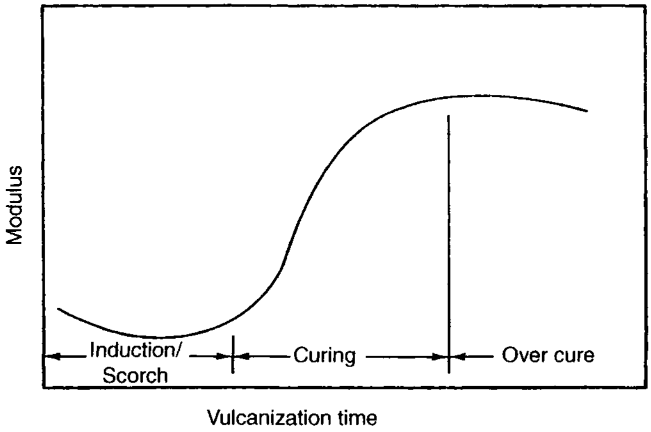


Figure 8.5 Steps in the vulcanization process.

induction period, 2) curing or cross linking stage and 3) reversion or over cure stage. The location of these three stages in the vulcanization cycle is shown in figure 8.5.

The induction period represents the time at vulcanization temperatures during which no measurable cross linking has occurred. It is a flow time in the plastic stage of rubber having apparently no or least modulus values of an un-vulcanized rubber. It is of practical importance since its duration determines the safety of the stock against scorching during the various processing steps which precede the final vulcanization. A Mooney viscosity test conducted at processing temperatures gives an excellent indication of scorch time. Following the induction period, cross linking proceeds at a rate which is dependent on the temperature and the composition of the rubber compound. When cross linking proceeds to full cure, continued heating produces an over cure which may result either in a further stiffening or softening of the compound. In the development and production of rubber compounds the rubber technologist strives to arrive at a balance between a tendency to scorch and a vulcanization rate which best fits the processing and cure requirements of his final product.

8.13 Vulcanization Test

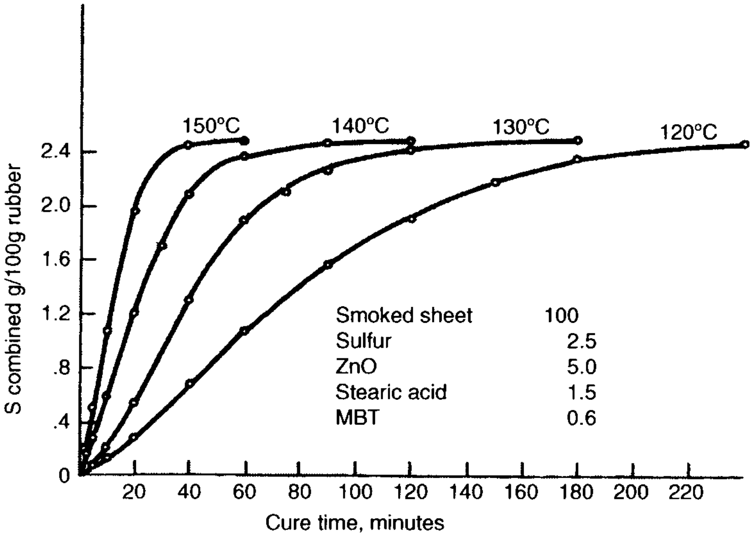
Vulcanization tests are aimed at determining the behaviour of the compound during these three phases of vulcanization cycles.

There are three techniques currently used for measuring and following the development of the properties during the vulcanization process.

- Chemical methods.
- Physical methods.
- Continuous measurements with the help of cure meters.

8.13.1 Chemical Methods

Since in a normal vulcanization system at least part of the sulphur combines with the rubber during vulcanization, an obvious way of following vulcanization is to measure the decrease in free sulphur. This method is not used extensively since it is well known that the combination of free sulphur does not correlate well with the development of cross links or other physical properties. In addition to this the analytical procedure is lengthy and costly. However free sulphur determinations are often made on finished products as a means of checking for uniformity of the product and to estimate the degree of cure. Figure 8.6 below shows the rate of sulphur combination at different vulcanization temperatures for a typical



Smoked sheet	100
Sulfur	2.5
ZnO	5.0
Stearic acid	1.5
MBT	0.6

Figure 8.6 Effect of temperature on rate of sulfur combination.

natural rubber compound. They exhibit the typical sigmoid shape ('S' shaped) which typifies all cure curves.

8.13.2 Physical Test Methods

The classical means for following vulcanization by physical methods is to vulcanize a series of sheets for increasing time intervals and then measure the stress strain properties of each and plot the results as a function of vulcanization time. A modification of this test generally called a rapid modulus test is widely used in the industry as a production control test. A single sample taken from a production batch of compounded rubber is vulcanized at a high temperature and its tensile modulus is measured. Temperatures as high as 380°F are used to reduce the vulcanization test time to only a few minutes. Any modulus value deviating from a predetermined acceptance limit indicates that the batch is defective and is to be rejected.

In all the above methods, it is necessary to cure specimens of test samples for each of a series of curing times and then perform the desired test on the vulcanizate. However, in the test for continuous measurement of vulcanization complete information could be obtained with saving in time. The mooney viscometer test approaches this objective. However a weakness of the mooney viscometer test is that the test is completed before a measurable modulus value after the scorch point has been obtained. This is because the test sample is destroyed after the induction period is passed due to tearing by continuous rotation of the rotor whether small or large. To overcome this deficiency and to provide a total cure curve for the entire vulcanization cycle, a series of instruments called cure meters was developed. In each of these instruments the stiffness or modulus of the compound was chosen as parameters for vulcanization continuously. The Vulkameter developed by Bayers, Germany was the first of the cure meters developed.

The functions of a rubber laboratory is to perform tests for:

- Quality control of incoming raw materials.
- Quality control of in-process stock.
- Quality control of finished goods.
- Providing technical service to the factory operators.
- Providing technical service to the customers.

- Preparing samples for market promotion.
- Development of compounding.
- Research.
- For assisting marketing department.
- Product performance; tests under simulated service conditions.

The above are generally classified as compliance to specifications, quality control, and research and development. Specifications are requirement for an end product. Control tests are conducted by rubber product manufacturers and research and development tests are conducted for acquiring more information about processes, products, applications development and raw materials. The physical testing of rubbers often involves application of a force to a specimen of rubber and measurement of the resultant deformation or conversely application of a deformation and measurement of the required force.

The stress strain test in tension including ultimate tensile and elongation is probably still the most widely used test in a rubber laboratory. The purpose of these tests is to ensure that all compounding ingredients have been added in the proper proportions, to determine the rate of cure and optimum cure for experimental raw materials including raw rubbers and compounds, for specification purposes and to obtain an overall quality check on the compound. Fewer tensile tests are conducted these days for these principal reasons: 1) cure meters give large data on state of cure and 2) more emphasis is given to the desired functional properties of rubber than the general quality. High tensile strength is seldom required in service and by itself it does not guarantee the level of any other property. However, a single test in a tensile machine gives modulus at specified elongation, ultimate elongation and ultimate tensile strength. The standard methods of physical testing are given in many national and international standard specifications such as American Society of Testing Materials (ASTM), British Standards (BS), and International Standards Organization (ISO) and a full description of these tests and their methods is not given in this book.

Rubber can be used by an engineer as a liquid latex or as a raw rubber or a vulcanized rubber. The vulcanized rubber can vary from soft gum stock through various stages of reinforced rubber (the state of which is achieved both by compounding techniques and by insertion of reinforcing materials such as fabrics, steel cord etc., thus making a composite material) to hard rubber which is called ebonite. The properties of metals can be varied by heat treatment but not to the same extent as those possible with rubbers. The most characteristic property of rubber is the enormous elastic strains to which it can be subjected without rupture. Any plastic material also can be stretched without rupture but without returning to its practically original length when the stretching force is removed. Therefore, it is obvious that rubber alone is resilient and most of the uses availed of rubber in the mechanical and process industries depend upon this resilience. First and foremost, resilience is an inherent characteristic of rubber. The degree of resilience may vary between both natural and synthetic rubbers. Resilience also depends upon the composition of the rubber compound. Certain compounding ingredients depress resilience. They do so by introducing internal friction. Resilience also depends on temperature. In general lowering the temperature reduces the resilience. Because of the interdependance of most of the physical properties such as tensile strength, hardness, tear strength, abrasion resistance and modulus, it has been observed by users of rubber that resilience is the best property most compatible with other properties, especially modulus. However there can be exceptions to this in case of products which exhibit high hysteresis loss.

The fundamental rubber properties vary from stock to stock and type to type and cannot have reproducible values. The chemical as well as mechanical engineer is accustomed to talking about the strength or impact strength or hardness of the rubber material as the inherent property possessed by the same. But in the case of rubber, owing to its enormous deformation capability, it is continuously changing during testing. One can observe during the tensile testing that the rubber sample in the tensile testing machine, as it approaches the breaking point, is vastly different from the same rubber with which the test was started.

We cannot ascribe any absolute meaning to the physical test results which depend upon the conditions under which the testing is done. Tensile strength, for example, depends on the rate of stretch, type of sample, size and shape, whether a dumbbell or a ring, temperature, humidity and other factors. Most of the rubber tests, although given a simple name arbitrarily, do not measure any one single property, but a complex group of physical attributes of rubber and should be only compared with similar rubbers being tested under the same conditions. In many industrial situations an engineer and a rubber technologist do not understand each other since they speak the same technical language with quite different meanings. Resilience for an engineer denotes strain energy per unit volume. For a rubber technologist it is a measure of rebound properties. Modulus applied to metals means either the shear modulus or elastic modulus and is a ratio of stress and strain. Applied to rubber, modulus means a stress to cause a somewhat arbitrary elongation and is used as a colloquial synonym for stiffness. Flexure means for an engineer bending but a rubber technologist calls it a static fatigue.

For many years, treating rubber with chemicals was considered as a test for rubber. The aim of testing was to find out its characteristics and when there was inadequate supply of the natural rubber to find out equivalent for the same. Testing was a part of research and development. The extraordinary properties of rubber, like its stickiness, elasticity and elongation encouraged researchers to conduct various tests on rubber to explore its then unknown characteristics, like measure of strength, reactivity with other chemicals, swelling in solvents, oxidatability, stability, etc. The chemical analysis of rubber provided the chief means of measuring the changes in rubber brought about by vulcanization. Even well before the discovery of vulcanization by Goodyear, the effects of heat, light and acids and alkalies on rubber were studied. Testing became necessary when early investigators faced a problem with rubber and its vulcanizates. Perhaps the earliest chemical resistance test on rubber could be by Charles Goodyear when he treated nitric acid with rubber which yielded a hardened mass. He mistakenly called this phenomenon vulcanization before he accidentally discovered vulcanization with sulphur. Chemical tests on rubber gave many clues as to its behaviour with acids and alkalies, products of reaction with oxidizing chemicals, etc. Though efforts towards conducting tests and designing testing devices were being undertaken, they were seriously limited by lack of knowledge about rubber and absence of suitable facilities for assessing and interpreting the investigations. Since the composition of the rubber being tested was not known, the results were misleading and investigation could not correlate the tests with the actual service life of rubber.

The physical tests conducted on rubber in general can be grouped into two classes according to Arthur W. Carpenter of M/s. Goodrich Company, Akron, Ohio a few decades ago. The first one includes measurement of dimensions, specific gravity/density tensile strength and ultimate elongation, the relationship between stress and strain, compression strength, hardness and resilience. These tests characterize the rubber vulcanizate and the test data usually represent a specification for the given rubber product. In the case of anticorrosive and anti-abrasive rubber linings, the above tests are quoted as the technical data. These tests are quite useful for compounding studies.

The second class includes tests for ageing, oxygen and ozone attack, adhesion, resistance to wear and tear, fatigue, etc. This class also includes tests under simulated service conditions under laboratory environments and immersion in fluids. These two classes of tests are conducted on vulcanized rubber.

In the case of rubber lining, a visual check with regard to the appearance is first done to find any air blisters or cracks on the cured rubber lining. A visibly good surface may still have a loose bond with metal which can be arbitrarily tested by giving small hits on the surface with a wooden mallet and comparing the sounds. A clear well-bonded lining may produce a clear defined sound. A surface with air blisters or loose bonds will give a clapping sound. Spark testing is the test for checking the continuity of lining.

8.13.3 Chemical Tests

Chemical tests such as acetone extract, chloroform extract, potassium hydroxide extract, free sulphur, total sulphur and combined sulphur are conducted to find out the ingredients admixed with rubber. Most of the physical and chemical tests and their methods are given in standard specification of ASTM, B S and other national and international specifications.

8.14 Density of Solids

Densities of common engineering materials reflect the mass and diameter of the atoms that make them up and the efficiency with which they are packed to fill space. Metals, most of them, have high densities because the atoms are heavy and closely packed. Polymers are much less dense because the atoms of which they are made (carbon, hydrogen and oxygen) are light and because they generally adopt structures which are not closely packed. Ceramics – even the ones in which atoms are packed closely - are on an average a little less dense than metals, because most of them contain light atoms like oxygen, nitrogen and carbon. Compounded rubbers show densities based on the densities of the ingredients which are mixed with them. Density or specific gravity measurements are important tests on compounded rubbers, especially those for lining applications, because volume cost is an important factor in these compounds and also these measurements reflect approximately the filler types used in the compounds.

8.15 Hardness

The most practical tests specifically followed for rubber lining are hardness test, spark test and immersion test. Hardness test is invariably the most frequently prescribed test for rubber lining quality by clients, though it is an inadequate test. The term hardness is a vague one; the different expressions such as "Scratch Hardness","Cutting Hardness" "Abrasion Hardness" etc. illustrate that different concepts of hardness exist.

Mohs developed his scale of hardness ranging from talc to diamond with the state of liquidity as the zero of the scale but did not define hardness. This hardness is indicative of the abrasive nature of the material when in contact with rubber.

Osmond defined hardness as that property possessed by solid bodies in a variable degree to defend the integrity of their form against causes of permanent deformation and the integrity of their substance against causes of division. This definition includes the idea of wear and is more applicable to metals than to rubbers.

In rubber testing the elastic structure is not damaged and the original shape is restored, since the deforming forces are lower than the recovery forces which are exerted by the elastic nature of rubber. In this respect rubber test methods differ from those applied to metals, bitumens, waxes, greases and ceramics where measurements are made of permanent deformation.

As the rubber hardness is a measurement of almost completely elastic deformation, it can be related to elastic modulus. Most rubber hardness tests measure the depth of penetration of an indentor under either a fixed weight or a spring load, and when rubber is assumed to be an elastic isotropic medium, the indentation obtained at small deformation depends on the elastic modulus, the load applied and the dimensions of the indentor. Scott showed that with a spherical ball indentor the relation between the indenting force D and the Young's modulus E was given by $D = ER^2 f\,(H/R)$ where R is the radius of the ball, H the depth of indentation and $f\,(H/R)$ is the function of the shape factor H/R which is characteristic of the shape of the indentor.

The standard test method for measuring the durometer hardness of rubbers according to ASTM D2240 – 75 is based on the penetration of a specified indentor forced into the material under a specified condition. The indentation hardness is inversely related to the penetration and is dependent on the elastic modulus and viscoelastic behaviour of the material. This method is an empirical test intended primarily for control purposes. No simple relationship exists between indentation hardness determined by this method and any fundamental property of the material tested. The real objective in conducting hardness tests is to measure the elastic modulus under conditions of small strains. In almost all hardness measuring instruments, the time at which the reading is taken is important, since for a particular set of conditions the usual hardness test imposes a constant load on the specimen; the test becomes creep test if readings are taken at different time intervals after application of the load. This factor is responsible for the failure of exact correlation between different instruments which require different time intervals for reading. This correlation is particularly poor when materials having varying creep rates are compared. The hardness of rubber vulcanizates changes with temperature and, therefore, it is important that tests for specification purposes or in different laboratories should be made at the same temperatures.

Buist and Davies during a study of natural rubber and chloroprene rubber stocks containing various carbon blacks point out that certain properties are closely related. For example, for natural rubber the following groups are highly correlated.

- Shore hardness, abrasion resistance.
- Swelling in benzene, elongation and modulus at 300%.
- All tests of hardness.
- Plasticity, compression, resilience and modulus.
- Shore hardness tests with all other tests.
- Tensile strength is not highly correlated with any other properties.

8.16 Spark Testing

Before an item of equipment lined with ebonite or any soft rubber leaves the workshop it is tested for non-porosity. According to regular practice, the only reliable method of determining this is that which makes use of a spark tester or inductor and a test voltage of 20,000 to 25,000 volts. For this purpose the spark tester or the inductor has been proved successful.

Spark testing is an important test which is conducted for continuity of rubber lining, as any faults at joints or pinholes in the sheets are detected with the spark testers. The adhesive strength to the metal can only be tested on counter samples lined and cured along with the rubber lined tanks. Destructive testing is not normally done with cut samples from the lined tank excepting a substantially aged tank, say after 10 years. Since rubber lining is a manual work a large surface area, say, of a ship tanker with more than 5000 sq meters can take about two months for completion under normal conditions. The shipyard or the client's site has to supply electricity, transport facilities, storage facilities, air, water and steam supply facilities in a nearby source. It is preferable that the rubber lining applicators arrange their own scaffolding, since this is a special arrangement with respect to lining operations of large tanks. The principle of the spark tester depends on the transformation of the primary voltage of 42 volts to one of 20,000 to 25,000 volts.

8.16.1 Description of Apparatus and Method of Test

The spark test equipment consists of a main or DC operated generator or interrupter, to which is added a Tesla coil within tuned circuit. The coil operates at its best at a fairly high frequency and is capable of generating a very high peak AC voltage. For testing rubber linings for the presence of any pinholes which pave the way for acid flow up to the metal surface beneath and corroding the same, an AC high voltage and high frequency spark discharge of 150 to 30,000 cycles / second should be used. The adjustment of the test output voltage is achieved by measuring the length of the spark in air by means of a spark gap of 20 to 25 mm. It is advisable to avoid excessively large electrodes due to the AC inductive loss through the thin anticorrosive coating of film thickness of 300 to

400 microns. So, the larger the electrode, the more diminished is the initial preset applied voltage. This inductive loss is not too critical when testing large joint-free lining surfaces, since for this type of application excessive large voltage is unnecessary for any porosity or faults present would be directly through the thickness of the lining material such as 2mm, 3mm or 5mm. A straight or T-shaped electrode with at least a 150mm to 200mm wide working probe edge is recommended for this type of testing.

For testing overlap joints, a pointed or tipped electrode should be used to ensure a minimum loss of applied voltage and thus maximum effective test concentration. It is important when testing joints to employ a sweeping down movement, continually moving, never stopping too long in one position. Otherwise too much strain will be applied to the dielectric strength of the rubber joints and adjacent areas of the joint, thus increasing the risk of dielectric breakdown. For pipes, an electrode of circular wire is used. Electrodes are available having both a flat section for flat surface and tips for joints. With surfaces having no faults/pinholes a bluish corona discharge will be observed in the electrode. Faults/porosity/pinholes will be recognized by the passage of a bright spark and the dying out of corona discharge. In addition an audible change of note will be heard from a buzzing corona, to a crackling noise with each spark drawn to the fault. Spark testing can cause more damage and leaks than it may discover if done improperly. One of the biggest mistakes is made when specifying the voltage. If the voltage is too high it can cause leaks, if too low it will not find leaks. The proper way to spark test is to calibrate the voltage to a known leak.

While using the spark tester, it is necessary to ensure that the probing brush or tip does not remain continuously in one spot, to ensure that a burnt hole may not be formed through the lining materials, because of the continuous sparking. The test voltage has to be adjusted to levels of lower than 10,000 while testing compounds with high loadings of carbon black and/ or graphite.

The following guide should be used while inspecting and spark testing of rubber lined tanks.

- A complete check against all rubber lining details on customer drawings and specifications should be made to ensure the rubber lining has been applied to the proper areas and with the correct gauge stock.

- General appearance should be observed and noted.
- All lap joints should be closely inspected for looseness and uniformity.
- Detection of trapped air can be accomplished by holding a light near the surface.
- While looking down the stock face for shadowed areas, if these are found, they need to be rolled down while bleeding the air with a needle or cut out to remove all trapped air and patched.
- Spark testing should be performed by qualified persons with a high frequency
- spark tester set at the recommended voltage, depending on the lining being tested.
- If a leak is detected, this area should be marked and patched prior to curing. When a rubber lining is patched prior to being cured it is considered an overlay. Overlays can be considered identical to a lap seam.

8.16.2 Probe Shape in Spark Testing

The probe shape is very important. The wand should be "L" shaped, measuring 12" on both sides of the "L." This will allow coverage of 12" per pass with the wand. The wire diameter should be approximately 3/32", with a 1/2" radius at the bend. Also, the tip should be turned up to eliminate the end discharge. On the intricate parts of the configuration, a fan probe is recommended, similar to a snare drum brush. Care should be exercised not to stop and concentrate on any one area. The wand should be passed over the rubber in a continuous sweeping stroke, approximately 10 inches per second.

It is imperative to proportion the spark voltage settings to the thickness of the lining to be tested. The following range of voltage is recommended as a starting point for calibration:

1/8" (3.2 mm) 6,250-8,500 volts minimum

3/16" (4.85 mm) 10,000-12,500 volts minimum

1/4" (6.4 mm) 12,500-15,000 volts minimum

Materials such as neoprene and graphite loaded linings require even lower voltage ranges; 7,500 volts for 1/8" and 3/16", and

10,000 volts maximum, for a 1/4″ thickness. Spark testing should be done only when it is considered necessary. Frequent spark testing leads to extensive repair work. Used linings generally have less electrical resistance, especially after several years of service. Where the salts have saturated the surface, or the solution has penetrated the lining, spark testing becomes more sensitive. Cracked linings also have a loss of thickness in the cracked area. Spark testing here must be done with extreme caution, with the lowest voltage necessary to produce a spark. Always remember to keep the spark testing equipment moving constantly, as it could burn through the lining and leave leaks if left in one place.

8.17 Immersion Test

Guidance with respect to the chemical resistant nature of rubber compounds can generally be obtained from the change rubber undergoes after immersion in liquids of various kinds. During immersion in a given liquid, the surface layer of the rubber is attacked immediately in the initial stages. The action of corrosive liquids such as acids, alkalies, water and fumes and gases basically involves:

Absorption
Diffusion
Permeation
Extraction and
Chemical reaction

Absorption leads to swelling or increase in weight. Diffusion leads to percolation through pores. Permeation leads to leakages of fumes and gases. Extraction leads to reduction in weight. Chemical reaction either adds to the weight or degrades rubber depending upon the intensity and vigour of the reaction and also the conditions to which the reaction product is exposed.

With swelling, the rubber is strained and its physical properties change. The leaching or extraction of certain chemical ingredients, especially the anti-oxidizing agents from rubber, has a significant influence on the useful life of the lining.

8.18 Specifications and Codes of Practice

A number of specifications and codes of practice are followed throughout the world, the major ones being ASTM, BS, DIN and JIS which give exhaustive information on rubber lining procedures, testing methods and code of practice. There are other standard specifications from various countries. The British Standard Institutions (BSI) BS 6373 (Lining of equipment with polymer materials for the process industries) deals with specification for lining with rubbers. It also specifies design, fabrication and surface finish of equipment to be lined, quality and methods of lining, inspection and testing, storage, handling, transportation and installation of lined equipment, testing continuity of lining and rectification methods for faulty linings.

The international standards for immersion testing of rubber deal with the change in weight and volume of rubber samples when they are immersed in various corrosive liquids. The details of these specifications are given below for reference.

Table 8.1 International standards for immersion testing of rubber

S. No.	Specification Code	Title
1	ASTM D471/77.52T Part 37 (American)	Test on Rubber property - Effects on fluid
2	B.S.903 Part A16 (British)	The resistance of vulcanized rubber to liquids
3	DIN 53521 (German)	Testing of Hevea rubber and determining the behaviour towards liquids, vapours and gases
4	JIS-KG 301 (Japan)	Dipping Test for rubber
5	ISO Recommendations R1817	Methods of tests for resistance of vulcanized rubbers to liquids

The chemical reaction of rubber lining with the corrosive chemicals and acids is much deteriorating to it, resulting in progressive damage of the lining, unless the reaction is not allowed to continue further. With increase in temperature the above changes take place at a faster rate. In all the above standard methods, the changes in weight of rubber after immersion in a liquid medium over a period of time and in different temperature conditions can be considered to be an indication for assessing its suitability for a given duty condition.

Though a standard norm or absolute reference value is not available for comparison in any of the international standard specifications and the technical and research publications with respect to the chemical resistance properties of rubber, liquid immersion tests certainly provide relative and useful data with which the suitability of anticorrosive rubber lining compounds can be assessed with a fair degree of accuracy. For this reason manufacturers and applicators of rubber lining resort to tests under simulated conditions instead of accelerated ageing immersion or swelling tests.

The above specifications give different temperature conditions for the liquid immersion test as follows:

B.S	25 +/– 1°C to 150 +/– 1°C
ASTM	–75+/–1 to 250 +/– 2°C
ISO	–75+/– 1 to 250 +/– 2°C
DIN	20+/– 2°C to 130 +/– 2°C

If temperatures are not specified in the specification, the immersion tests have to be carried out at room temperature. The volume of the immersion liquids should be adequate enough to immerse the sample of rubber. The test should be carried out in the absence of direct sunlight to avoid atmospheric oxidation. Test pieces from cut samples or counter samples from the finished rubber lining compound have to be buffed smooth.

The duration of the tests in the above standards vary as follows:

BS – 24 hrs, 18 hrs, 9]6 hrs, 168 hrs up to 30 days

ASTM – 22 hrs, 70 hrs, 166 hrs, 670 hrs

ISO – 22 hrs, 70 hrs, 7 days and multiples of 7 days 14 days and 28 days

The change in volume as well as weight of the test piece after immersion, with respect to time, is recorded. The test chemicals and reagents used in immersion test and the nature of attacks are as given in the table below:

Table 8.2 Reagents used in immersion tests

Name of chemical	Nature	Density	Main type of attack on Rubber
Water	Natural	1	Diffusion
Hydrochloric acid	Acidic	1.18	Diffusion and formation of reaction products
Sulphuric acid	Acidic	1.84	Diffusion
Phosphoric acid	Acidic	Depends on concentration	Diffusion
Nitric Acid	Acidic	1.42	Diffusion
Sodium Hydroxide solution	Alkaline	Depends on concentration	Diffusion

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9

Rubber to Metal Bonding

9.1 The Rubber Bonding Process

Rubber to metal bonding is a generic phrase covering a number of interdependent processes. The rubber bonded units that result from the process are used for the isolation of noise and vibration in automotive, engineering and chemical industry applications, such as in rubber lining of process equipment.

Although the birth of the rubber industry was over 200 years ago, it has only been during the last about 75 years that the design engineers have been able to combine the strength of metals with the elasticity of rubber. Rubber bonding was done by mechanical means. Probably the first real bond between rubber and metal was achieved through hard rubber technique [1]. The first commercially successful bonding process was achieved by brass plating technique during the 1920s. In this process the ratio of copper to zinc in the brass was maintained to a specified level for achieving proper bonding properties. Compounding of rubbers for bonding with brass plating technique had severe limitations and as such this technique has become outdated. By the end of World War II, bonding with chemical agents began gradually to replace all earlier processes. Hard rubber or ebonite based bonding systems are still followed successfully in applications like rubber rollers and tank lining.

Several years ago the subject was regarded as a "black art". Now the technology allows the production of a uniform, high quality product that is free from failure. Much of the science behind the technology remains cloaked in uncertainty, but it is sure to become an important part of future developments. Today, environmental concerns have an impact on all aspects of commerce. Rubber-to-metal bonding is no exception, so the process is changing to reflect these concerns.

In the chemical bonding technique, three essential elements form the core of the bonding process: the rubber compound, the bonding agents and the substrate. The selection of the polymer base and the associated compound depends mainly on the product specification. Provided that the rubber can flow without developing a significant level of cross linking (less than 2%, well before the onset of scorching), a bond can be formed using any rubber compound. There are no restrictions on the use of particular compounding ingredients, although it is best to avoid substances that will bloom rapidly to the surface of the uncured stock. The rubber chemist therefore needs to concentrate attention on matching the physical requirements of the cured rubber-metal product and the processing needs of the rubber lining or rubber covering process as well as other forming processes. It is generally agreed that bonding of rubber with metal occurs through both physical and chemical primary bonds. Metals being polar, rubbers will be more easily bonded to them. From this the concept of bondability index has been developed [2,3]. The following figure 9.1 shows the bondability index of some of the common rubbers. The higher the index, the more readily the rubber gives good bonding with metals when using a single coat adhesive system.

The lower the index the greater is the necessity for using a two coat system – a primer to give good bonding with metal and a secondary or top adhesive coat to give good bonding with rubber. Many bonding agents are available, the most important ones being: 1) polyisocyanates 2) chlorinated rubber and 3) phenol formaldehyde resins. Organic polyisocyanates such as triphenyl-methane-tri-p-isocyanate are useful for bonding natural rubbers to mild steel, cast iron substrates and light alloys. A solution in methylene chloride is sold as "Desmodur-R" by M/s Bayers, Germany. Other

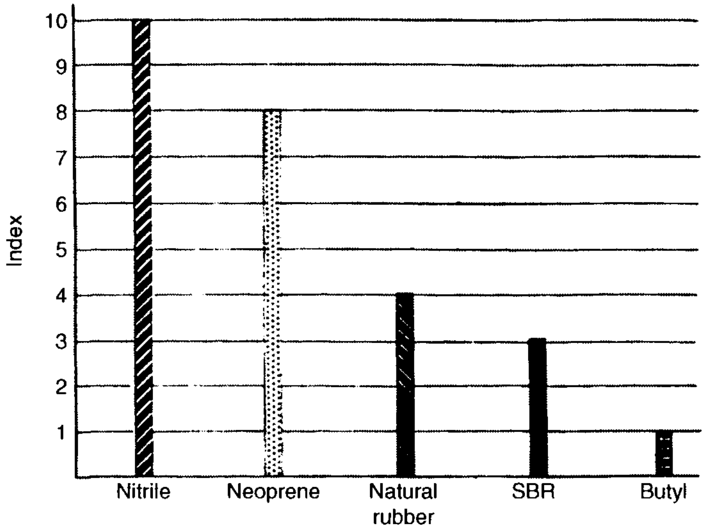

Figure 9.1 Bondability index of common elastomers.

brands are also available on the market. Chemlok brand adhesives based on isocyanates are manufactured by M/S Lord corporation USA and widely used. There is a tendency of the isocyanate adhesive to be squeezed out during the molding process under hydraulic pressure. This can be partially obviated by adding chlorinated rubber to the solution.

Chlorinated rubber is also an effective bonding agent. It can be used for bonding neoprene, nitrile and natural rubbers to metals. Phenol formaldehyde resins have been used alone or in conjunction with chlorinated rubbers, but curing time is lengthy.

9.2 The Bonding Layer

For several years the bonding agents have consisted of proprietary polymer/solvent solutions, with a primer coat based on phenolic-style resins and a topcoat formed from solutions of polymers and other ingredients. The formulation of these materials is not disclosed, but much patent literature is available. Bond formation appears to be associated with the development of a very high modulus layer in the rubber immediately adjacent to the surface of the substrate. The thickness of the layer is of the order of 15 μm and varies according to the nature of the rubber formulation and the level of an ingredient named as di-nitroso-benzene (DNB) in patents.

9.3 Selection of Bonding Agents

The selection of bonding agents depends on the type of rubber to be bonded, the modulus of the rubber and the component design. The selection process is critical to the robustness of the bonding process. In the past decade water-based versions of bonding agents have been introduced, which after much development are now effective replacements for the solvent-based bonding agents. Bonds tend to be up to 10% lower, but components show good resistance to the usual environmental conditions found in automotive applications. The application methods for water-based bonding agents are similar to those for the solvent systems, but inserts do need to be preheated to 60–80°C before spraying with the primer, and reheated before applying the topcoat. Drying times are surprisingly quick and are no barrier to high volume production.

9.4 Choice of Substrate

The choice of substrate rests solely with the component designer, who must consider the necessary strength and durability requirements for service use. The traditional substrate is steel, in all its forms and grades, Use is also made of aluminium alloys and polyamides to save weight. Almost any material can be bonded to rubber, provided that it can withstand the heat and pressures of the rubber manufacturing process. For practical purposes this eliminates polyolefin plastics. PTFE can be bonded successfully to the rubber by chemically etching the surface of the plastic prior to application of the bonding agents. However, its use in such applications has been largely superseded by woven PTFE/Terylene fibre material, which offers a mechanical bond, and, more recently, by slip agents that bond freely to the surface.

9.5 The Bonding Process

The first key step in the preparative process for the metal is cleaning. To prepare steels, all traces of oil, grease or solid lubricant must be completely removed from the metal surface. Degreasing and shot blast are widely employed, although wet blasting followed by a phosphate conversion treatment is gaining greater acceptance as a cost-effective process for small component mouldings, and it gives the added benefit of improved corrosion resistance. All emissions from this process can be contained and process media recycled, making it more environmentally friendly

Whatever process route is taken, the emphasis has to be on control to ensure consistency of results. Degreaser plants need to be regularly monitored to minimize any buildup of contaminants or change in pH. The grade of grit used in shot-blast operations is important and will affect the environmental resistance of the finished product. The profiling of particle sizes is a useful tool to monitor machine effectiveness and ensures that dust levels remain low. Routine sampling will show if fresh grit is being fed to the machine and detect a failure of the dust extraction mechanism. Differences in surface profile due to changes in the size range of the grit will not cause bond failure, but the presence of dust and debris in the grit will. Dust adheres to the newly cleaned metal surfaces and is very difficult to remove, even with a second degreasing operation.

9.6 Application of Bonding Agents

The methods for applying bonding agents are subject to continual review. The process requires the application of a grey primer coat and a black topcoat. In high volume production methods, problems with blocked guns or other mechanistic faults may allow components to be produced without primer below the topcoat. Such parts will initially show a good bond but will be likely to fail in service. Various foolproof means to prevent this happening have been suggested, but are yet to be proven in use. The best method to date is to ensure that the primer is sprayed over a slightly wider area than the topcoat so that a witness to the primer exists. However, this does not work for metals which need to be bonded over 100% of their surface

As for solvent systems, a barrel spraying machine may be used for surfaces that need to be coated on all areas. The Environmental Protection Act has prompted manufacturers to find means of reducing or eliminating the volume of solvent used in cleaning and coating processes. The introduction of low pressure, high volume (LPHV) spray guns reduced the volume of bonding agent used by 20%.

In the case of rubber lining of tanks, adhesives, prepared in the sigma-mixture, are tested for their viscosity and homogeneity, before applying onto the surface of the vessel to be lined. It is usual to give a first and primer coat of the adhesive over the blasted surface immediately after sand blasting. Coating is done by brushing

Generally for lining and other interconnected operations, the humidity should not be very high. The preferred humidity is 60–70%. To enhance good adhesion, several primer coats are used on the metal surface. After coating, it is dried before the actual lining process, i.e., the application of calendered sheet. It is necessary to ensure that the solvent in the adhesive has completely evaporated as otherwise, during lining, the volatile solvent will "blister" out thereby making the bonding poor.

9.7 Adhesive Manufacture for Ebonite Bonding

Sigma blade mixture/ kneader is used for preparing the adhesives used for lining using ebonite bonding technique. Warmed stocks in the mill are charged into the mixer, along with solvent and other ingredients, and then the mixer is run for a cycle time, which can vary between 4 hours and 16 hours. When the adhesive made is homogenous, it is tested and packed in barrels to be later used for lining. Further, before lining the adhesives are tested for any degradation in their properties as a precaution.

As the choice of raw materials is steadily becoming a complex task with new polymers and compounding ingredients fighting for a place among the already established ones, critical evaluation is essential before their worth is assessed.

It should be recognized that appreciable shifts in bonding strength are sometimes made possible by special compounding variations; for instance, the heat resistance of NR vulcanizates may be improved considerably by variation of the vulcanizing system. The normal sulphur vulcanization system is capable of many variants, which will govern the chemical nature of the sulphur cross link, i.e., whether it is essentially a more, di, or poly-sulphide type. The nature of sulphur cross link can have considerable influence on the bond strength and the heat-resistance of vulcanizate

For a particular application, the base polymer, or when desirable and possible the polymer blend, has first to be selected according to the broad pattern of final properties required and the curing method decided. This must then be combined with an appropriate cross linking system, and whether black or non-black, the reinforcement, if any, has next to be decided, sufficient processing aids being included to ensure satisfactory mixing and processing. It should be remembered that reinforcing fillers of finer particle size are, as a rule, generally expensive and so excessive reinforcement should be avoided when not critical while designing bonding adhesive formulations. Any permissible diluents or special additives for specific effects are then added to the formulation list.

Protective anti-degradents are selected according to the severity and type of service exposure and to their relative effectiveness in the particular base polymer used. The stages in which the formulation are mixed in production must also be borne in mind, and the appropriate ingredients grouped accordingly. For example, protective agents are commonly added early and cross linking agents last.

9.8 Moulding of Rubber-Metal Bonded Product

The rubber moulding operation brings together all the elements of the process. It is the most critical point in the process of manufacture of rubber-metal bonded components. If one element in the production cycle goes wrong, then the product is destined to fail. Moulds do need to be designed to ensure exact balance between cavities and the elimination of trapped gases. The presence of gases causes a high incidence of bond failures through the "diesel effect," whereby elements of the bonding agent film burn under the combined effects of heat and high-pressure gas. Lack of balance between cavities will result in some components that are imperfectly formed and give rise to bonds that may fail.

Problems such as these are readily avoided by study of the rubber flow through the mould using computer flow simulation packages. These model the effect of mould design on pressure gradients and the cross linking behaviour of the rubber. Factorially designed experiments, using the computer model, allow the optimization of runner sizes and moulding conditions before the mould is manufactured, so that components are produced to specification when the mould is first used.

9.9 Compounding of Rubber for Metal-Rubber Bonding

Compounding is the most important aspect in achieving a good bond. Its importance now is not overlooked as before, when the focus was on adhesive systems and substrate profiles which are no doubt essential elements for a good bond. Very often small changes in the formulation of a compound increases the level of bonding, starting from the types and dosages of antioxidants to fillers either inert or reinforcing. In order to attain strong bonds, it is essential to ensure one hundred percent wetting of the compounded stock with the adhesive cement, and the required proportions of the active ingredients are present without loss during mixing operations to enable primary chemical bonds to be formed. This means that at the time when the rubber metal interface is formed, there should be no sign of vulcanization. The curing system should be so designed as to give an optimum delayed action consistent with maximum productivity, and mixing conditions should be specified to ensure that this delayed action is consistent from batch to batch. A curometer trace is preferably to be obtained on each batch at the curing temperature as a quality control check.

As a rule-of-thumb, the higher the filler content the better is the rubber-metal bond and of all the fillers carbon black is the best. Wherever possible at least a 50 phr of carbon black is suggested for all compounds with suitable adjustments of dosage levels of other ingredients such as process aids, etc. This is not to say that one has to sacrifice other properties. In rubbers with high bondabilty index all kinds of carbon blacks can work equally well. However, channel blacks are the preferred ones for those with low bondability index. It is very important that softening or processing oils are chosen with extreme care. If the oil is not fully compatible with the rubber, bonding will be severely affected due to leaching out of the oil at the rubber/metal interface. Aromatic and ester type oils are generally unsatisfactory while best results could be obtained with naphthenic oils. Highly oil extended synthetic rubbers are not recommended for rubber-to-metal bonded products. Blooming ingredients should be avoided or their blooming effect reduced with low dosages. Pre-warming of the stock is a good practice to get a fresh bondable rubber surface. It has to be stressed once again that the most important aspect of compounding is to have sufficient delayed action to ensure that there is no onset of cure while the rubber/bonding agent interface is formed.

Another processing trick is that most chemical bonding or ebonite bonding agents being dispersions of insoluble ingredients, a homogeneous dispersion is made by stirring while applying to ensure uniform spread of the ingredients in the adhesive film. This is even more important if make-up diluents are used when settling of the dispersed ingredients come out as an additional problem. Regular checks on viscosity and solid content are suitable quality control measures to be adopted without omission.

Dipping method for adhesive coating of the metal discs is the best method for moulded rubber products manufacture while the quality control required is frequent checks on viscosity and solid content of the dipping bath. The later will be maintained by slow and constant agitation both vertically and horizontally in the bath.

For manufacturing reinforced inflatable products such as tanks and seals, fabric reinforcement is done with suitable adhesive dips onto the fabric. Aqueous synthetic latex and resorcinol formaldehyde adhesive solution is used as dipping solution for adhesion with rubber sheets for cutting blanks for feeding into the moulds. The adhesive is applied by passing the woven fabric through a dip tank and controlling the adhesive pick-up. The adhesive then is dried in an oven before applying the rubber sheet on the coated fabric either cotton or nylon.

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10

Vulcanization Technology

10.1 Principles of Vulcanization

It is essential to know at the first instance what qualities are desired in a vulcanizate, and in order to attain these properties, what would be the problems involved. As a practical approach, vulcanization is considered as a process whereby a material of different compositions and a bad conductor of heat is subjected to the process with an intention of producing a uniform product having improved physical properties. That such a result is obtained day in and day out with either natural rubber or synthetic rubber is a tribute to improved compounding ingredients permitting a wide range of cure without any deleterious effect and also engineering design which allows uniform heating. The possibilities of variables are so many in the process of vulcanization and they are so serious that it is important that utmost control is exercised on the quality of raw materials and the uniform dispersion of sulphur and other ingredients. Secondly a precise control of curing time, pressures and temperatures adopted in the operation is essential.

After the rubber compound has been properly mixed and shaped into blends for moulding, calendering, extruding, fabricated into composites or hand formed, lined on the tanks and vessels, etc., they should be either vulcanized in the autoclave or in press moulds. Press moulded components are made in hydraulic presses. In the former case one of the following methods would be necessary depending upon the size of the equipment and the compound formulation:

Autoclave curing
Open steam curing
Hot water curing
Self-vulcanizing
Cold bond lining and
Curing by using the vessel itself as an autoclave.

An autoclave is a pressure vessel, capable of withstanding an internal pressure generated by steam. See figure 10.1 below showing an autoclave erected outdoors with its door opened. Autoclave processing is the most common method used for curing thermoset products. The curing of thermoset composites involves both mechanical and chemical processes. Mechanically, pressure is applied to remove trapped air and volatiles, and to consolidate the individual plies and fibers. Chemically, a cross linking reaction must be initiated and taken to completion to form a rigid matrix. Cross linking is most commonly initiated through the application of heat, though it also may be initiated by exposure to ultraviolet light, microwaves,

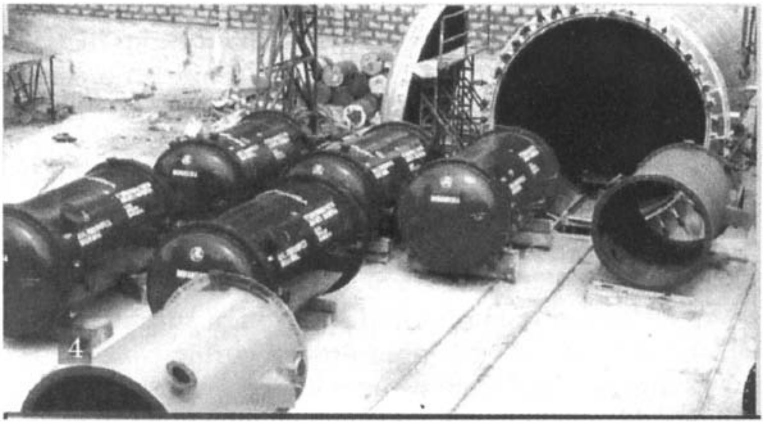

Figure 10.1 3 m × 8 m Autoclave Foreground-rubber lined and painted ducts with dished ends.

or high-energy electrons (e-beam curing). In the autoclave process, high pressure and heat are applied to the part through the autoclave atmosphere, with a vacuum bag used to apply additional pressure and protect the laminate from the autoclave gases. The cure cycle for a specific application is usually determined empirically and, as a result, several cure cycles may be developed for a single material system, to account for differences in laminate thickness or to optimize particular properties in the cured part.

The typical autoclave cure cycle for a fabric reinforced inflatable is a two-step process. First, vacuum and pressure are applied while the temperature is ramped up to an intermediate level and held there for a short period of time. The heat reduces the polymer viscosity, allowing it to flow and making it easier for trapped air and volatiles to escape. The plastic polymer also begins wetting the fibers at this stage. In the second ramp up, the temperature is raised to the final cure temperature and held for a sufficient length of time to complete the cure reaction. During this step, the viscosity continues to drop, but preset temperature ramp rates and hold times then stabilize viscosity at a level that permits adequate consolidation and fiber wetting, while avoiding excessive flow and subsequent polymer starvation. These control factors also slow the reaction rate, which prevents excessive heat generation from the exothermic polymerization process. An autoclave cured fabricated rubber inflatable acid storage tank is shown in the following figure 10.2.

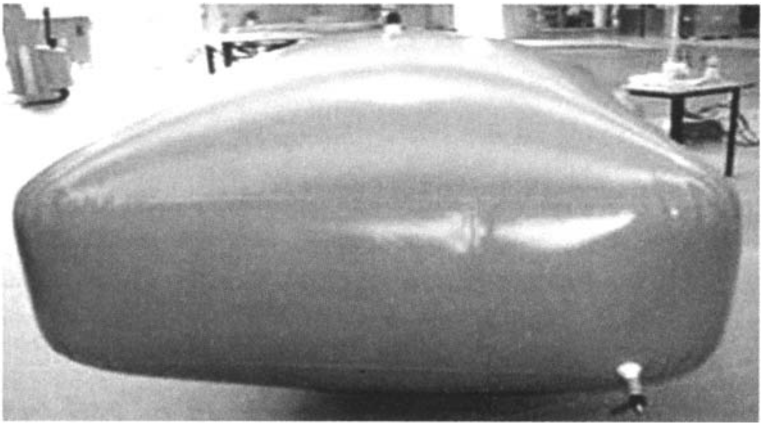

Figure 10.2 Fabric constructed rubber inflatable storage tank.

For rubber lined vessels, the working pressure in an autoclave is normally 4–5 kg/cm sq gauges. The autoclave selected for this purpose has to accommodate a fairly large proportion of chemical plant equipment, piping etc. The lined equipment is loaded in a trolley and then pushed into the autoclave with the help of a winch motor. The boiler pressure is maintained at 100 psig and the steam pressure inside the autoclave is kept at 60 psig, resulting in a constant temperature of 130°C to 140°C, as the case may be, depending upon the type of compounds used for lining. The curing cycle time normally varies between 6 hours to 16 hours, dependant largely on the compound used and the size of the vessel. After vulcanization is over, the autoclave is opened and the lined equipment and tanks are unloaded for finishing and inspection.

In the case of open steam curing and hot water curing, the rubber lined vessel is to be insulated outside to provide heat retention at the adhesive layer so that proper bonding of the rubber to metal is ensured. In the case of curing by using the vessel itself as an autoclave, the same is to be designed to withstand the temperature and pressure conditions of the curing process as well. This is to be ensured by the vessel / tank fabricator. It is a good practice to insulate the outside of the vessel while the lining is cured with steam. The pressure usually kept in this case is 1atm. Self-vulcanizing linings are not very popular except in the case of non-critical equipment. The cold bonding method involves the use of precured rubber and room temperature curable bonding adhesive. This method is mostly followed for large sized tanks.

During vulcanization the following physical and chemical changes occur.

- The long chains of the rubber molecules become cross linked by reaction with the vulcanizing agent to form a three-dimensional molecular structure. This reaction transforms the soft and weak plastic-like rubber material into a strong elastic resilient product.
- The rubber loses its original tackiness and becomes insoluble in solvents and is more resistant to deterioration and degradation effects of heat, light and ageing process.

The following vulcanization systems in the compounds are followed to effect the above changes.

10.2 Sulphur and Sulphurless Vulcanization

The most common rubbers used in industry are the general purpose synthetic types and natural rubber which contain adequate unsaturation. With these so-called diene rubbers, vulcanization with sulphur is possible. Sulphur is the most commonly used vulcanizing agent. With sulphur, cross links and cyclic structures of rubber molecules are formed. The total number of sulphur atoms combined in the cross link and cyclic structure network is usually called the coefficient of vulcanization [1] and is defined as the parts of sulphur combined per one hundred parts of rubber. For most rubbers one cross link for about each 200 monomer units in the chain is sufficient to produce a vulcanized product. In an efficient accelerated curing system, about 1 or 2 sulphur cross links with little or no cyclic group are formed. In an inefficient system of curing, the cross linked sulphur is equal to 8. The amount of cyclic and cross linked sulphur in the network govern the ageing characteristics of the rubber products. Vulcanization effected without elemental sulphur by the use of thiuram disulphide compounds which are accelerators of vulcanization, or with selenium or tellurium, produces products which are more resistant to heat ageing. With the thiuram sulphides efficient cross links containing 1 or 2 sulphur atoms are found and in addition to this, the thiuram accelerator fragments act as antioxidants. Therefore sulphurless or low sulphur cures with such accelerators produce products with better ageing characteristics.

10.3 Peroxide Vulcanization

The saturated rubbers such as butyl or EPDM cannot be cross linked by sulphur and accelerators. Organic peroxides are necessary for the vulcanization of these rubbers. When the peroxides decompose, free radicals are formed on the polymer chains and these chains can then combine to form cross links of the type where only carbon-carbon bonds are formed, unlike in sulphur vulcanization. These carbon-carbon bonds are quite stable ones. Such bonds are also formed by vulcanization using gamma or x-ray radiation of compounded rubbers. Some rubbers can be vulcanized by the use of certain bisfunctional compounds which form bridge type cross links, for example, neoprene with metal oxides or butyl rubber with dinitrozobenzene.

10.4 Vulcanization Conditions

It can be seen that every type of vulcanization system differs from every other type in the kind and extent of the various changes that together produce the vulcanized state. In the vulcanization processes, consideration must be made for the difference in the thickness of the products involved, the vulcanization temperature and thermal stability of the rubber compound. The word cure to denote vulcanization is believed to have been coined by Charles Goodyear and the same has been a recognized term in rubber industry circles [2]. The conditions of cure will vary over a wide range according to the type of vulcanizate required and the facilities available in a rubber factory. Many factors must be predetermined, including the desired hardness of the product, its overall dimensions, the production turnover required and the pretreatment of the rubber stock prior to vulcanization. Hardness will normally be determined by the composition of the stock but it can also be influenced by the state of cure.

10.4.1 Effect of Thickness

The thickness of the product is highly significant, due to the necessity of providing heat in the interior of the rubber and preserving a uniform state of cure through the cross section. Rubbers are poor conductors of heat and thus it is necessary to consider the heat conditions, heat capacity, geometry of the product in the case of mouldings and autoclave cured items, heat exchange system in the case of open steam or hot water cured processes adopted for rubber lined equipment and the curing characteristics of a particular compound where articles thicker than about one quarter of an inch are being vulcanized. It is a general shop floor practice to add an additional five minutes to the curing time for every one quarter inch thickness in the moulded articles. In the case of autoclave curing of lined tanks and vessels, a slow rise in temperature up to the curing temperature is the proper procedure when the thickness of lining is more than a quarter inch. For thicknesses larger than a quarter inch, say 2 inches or 3 inches as in the case of ebonite pipes and components, it is desirable to adopt hot water curing technique. Two practical methods of dealing with thicker articles are 1) step-up cures where more than one temperature is employed and 2) slow external cooling in place of slow heating. Heat is discontinued before the cure is complete and. the rubber is kept under pressure either in the mould or in the autoclave. An increase in dimensions necessitates a reduction in curing temperature with increased time to obtain uniformity throughout the product. However, low temperature cure in open steam may lead to plastic flow of the rubber, if onset of cure does not commence at that temperature. Suitable compounding technique is followed to offset this problem.

10.4.2 Effect of Temperature

The vulcanization temperature must be chosen in order to produce a well cured product having uniform and optimum physical properties in the shortest possible time. The term temperature coefficient of vulcanization can be used to identify the relationship between different cure times at different temperatures. With this information optimum cure times at higher or lower temperature can be estimated for many rubber compounds with known coefficient of vulcanization. For approximately most rubber compounds the coefficient of vulcanization is 2. This indicates that the cure time must be reduced by a factor of 2 for each 10°C increase in cure temperature or if the temperature is reduced to 10°C, the cure time must be doubled.

10.4.3 Effects of Thermal Stability

Each type of rubber has a definite range of temperatures which may be used for vulcanization. These temperatures may vary somewhat, but it is quite important not to exceed the maximum for each since some form of deterioration will occur. This effect is either shown by the appearance of the finished product or by its physical properties.

10.5 Techniques of Vulcanization

Numerous methods of vulcanization are available for manufacturing a rubber product. In the case of moulded goods for process industries, the methods followed are similar to that for other products except that the former may have a different compound formulation. The methods used in most industries are based on standard techniques universally followed which are briefly outlined below.

10.5.1 Compression Moulding

This method or a modification of it as required by convenience utilizes the most common type of mould used in the rubber industry. This is the standard method followed throughout the world and a vast assortment of moulded products known as general rubber moulded goods are cured in this method. Essentially this method consists of placing or loading into a two piece mould, a precut blank or a composite material and then closing the mould. The pressure applied by the hydraulic press forces the material to fill up the cavity in the mould bringing the required shape into formation and the slight excess rubber in the blank flows out of the rims of the mould or through vents. This excess rubber is known as flash. The common platen sizes range from 12″ × 12″ to 32″ × 32″ when the presses are operated by single hydraulic rams. When multi rams are involved, the platen size is unlimited and conveyor belts of even more than 30 feet long at a time are produced in larger platens. Such belts are fastened at the ends and cured in the presses to make them endless. For higher productivity the presses will have multi-day light platens. Usual hydraulic pressure applied during press cures ranges from 1500 lbs/inch to 2000 lbs/inch. Steam is the most often used heating medium although electrical resistance heating also is used wherever high temperature cures are required. For manufacturing rubber to metal bonded components, compression moulds are preferred. Shrinkage of cured rubber is an important factor when designing moulds. Shrinkage depends on the type of the rubber compound, type of the mould and the temperature of the cure. An arbitrary figure of 1.5% to 3% is chosen for general rubber moulded goods as shrinkage allowance.

Tyres are normally cured in a modification of the compression mould where a bladder or an inflated airbag forces and holds the green rubber stock of the tyre against the mould surface during vulcanization. This force reproduces the design of the tyre tread and the heat from the steam is introduced into the bladder to effect the vulcanization. Small size rubber expansion joints used in piping systems are moulded by compression moulding whereas larger sizes are hand built on moulds. and cured in autoclave. Thick ebonite mouldings are vulcanized by a step-up cure process.

10.5.2 Transfer Moulding

Transfer moulding involves the distribution of the uncured stock from one part of the mould called as pot into the actual mould cavity. This process permits the moulding of intricate shapes or the introduction of inserts like metals in many composite products. These procedures are difficult in compression moulds. Although these moulds are relatively more expensive than compression moulds, the actual process permits shorter cure times through the use of higher temperatures and better heat transfer which is obtained due to higher pressure applied to force the compound into the mould.

10.5.3 Injection Moulding

This method is normally followed for plastic products. However the same with modifications of equipment is adopted for manufacture of small rubber components. By careful control of the feed stock the rubber products can be vulcanized in less than several minutes. This method can be completely controlled by proper feed, injection and demoulding cycles resulting in low rejection rates and lower finishing costs.

10.5.4 Open Cures

Hot air ovens can be used to vulcanize thin articles and sheets which have been pre-shaped in extrusion process or calendering or by a combination of precuring in a mould followed by post curing. Post curing is done to remove decomposition products from products cured with peroxides. This system is not very efficient due to the poor heat transfer of hot air. Longer cure times at lower temperatures are necessary to prevent the formation of porosity or deformation of the unvulcanized or still to be vulcanized rubber stock. Hot air cure is divided into open air cure at atmospheric temperature and cure at closed ovens. The usual conditions are an air cure rising from 80°C to 120°C within 45 to 60 minutes. Hot air cured vulcanizates give a glossy finish.

Open steam can be used in closed vessels, the autoclaves. The process involves using saturated steam under pressure. The saturated steam acts as an inert gas and better heat transfer is obtained and thus high temperatures can be employed and shorter cure times are possible, making the process more desirable than hot air ovens. Dry steam under pressure is used in horizontal heaters. Hoses, cables, rubber lined equipment, rubberized rolls, extruded profiles and calendered sheets are cured by this method. In the case of rubber sheetings for lining, a cloth liner is used as a backing while winding them on drums and these liners are wet and exert pressure when dried up and due to shrinkage. Sheets of 10 to 12 m long are wound over hollow drums to a thickness of as high as 40 to 50 mm and tightly wrapped with wet gada cloth liner. This method has not been replaced by any other newer methods to any extent. The use of open steam for vulcanizing rubberized fabrics is the most efficient method. The inflated fabrics are kept during cure in their normal inflated shape. The inflated pressure is kept up to balance the internal and external pressure of the steam. Near the completion of the cure air is allowed into the steam to give a steady and slow drop in pressure.

Hot water cures can be used for articles that are not affected by immersion in hot water. This method is useful for thick walled articles and rubber lined equipment and especially most suitable for ebonite compositions. Direct contact with water produces better heat transfer than with hot air or steam. Consequently this system gives less deformation of products during cure.

10.5.5 Continuous Vulcanization System

This system involves the use of some form of heating by air or steam in a chamber in a manner such that the vulcanization occurs immediately after the rubber is formed in an extruder or calender. This is a suitable process for extruded profiles and calendered sheets and conveyor belts. Liquid curing method (LCM) is also a continuous process which involves the use of suitable hot liquid baths in which extruded profiles can be passed through and vulcanized continuously. Items can be cured rapidly at temperatures from 200°C to 300°C; however the compounds must be suitably designed to prevent porosity as this is a common problem with any extrudate. Suitable materials for curing medium includes bismuth-tin alloys, an eutectic mixture of potassium nitrate and sodium nitrate (an eutectic is a mixture of two or more constituents which solidify simultaneously out of the liquid at a minimum freezing point), polyglycols and certain silicone fluids. Fluidised beds consisting of small particles (glass beads) suspended in a stream of heated air are an efficient vulcanization system. They are normally used for continuous vulcanization of extrusions. The heat transfer is approximately 50 times greater than with hot air alone.

10.5.6 Cold Vulcanization

Thin articles may be vulcanized by treatment with sulphur monochloride by dipping in a solution or exposure to its vapours. This process has been replaced by using ultra accelerators which are capable of curing at room temperature.

10.5.7 Cure with High Energy Radiation

Systems using either gamma radiation from cobalt 60 or electron beams have been used for vulcanization. The electron beam method has been used for curing silicone rubbers.

10.5.8 Optimum Cure

Determination of optimum cure and rate of cure are essential prerequisites in the selection of stocks for a particular finished product. These are generally obtained by first curing the samples at say 140°C and determining the modulus, tensile strength and hardness at various cure times. The optimum cure is normally fixed by plotting modulus, tensile strength and hardness against various cure times. Optimum cure may also be fixed on the basis of other properties such as tear strength, abrasion resistance or resistance to flex cracking. In the US the optimum cure is mainly based on optimum modulus. In Great Britain optimum tensile strength is the one followed for determining optimum cure. A cure rate chart of practical vulcanization is shown below in figure 10.3 comprising three curves based on three physical determinations, namely ultimate tensile strength, 300% modulus and hardness together with one based on chemical determination, namely free sulphur in the vulcanizate. The point of optimum cure is taken from the three physical properties from the graph.

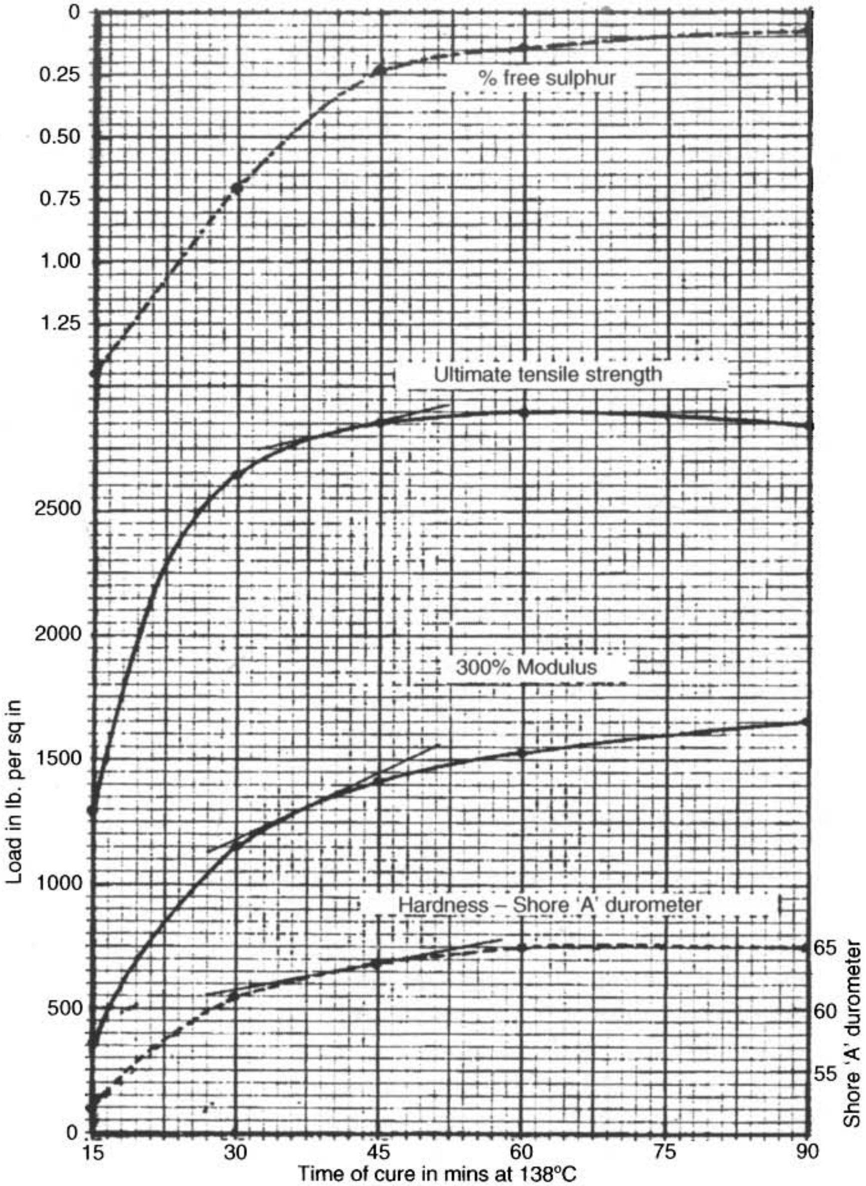

Figure 10.3 Practical vulcanization chart for optimum cure.

1. Tensile strength
   The point on the curve which has a tangent based on a slope of 10 lb increase in tensile strength per minute of cure denotes an optimum cure time of 46 minutes.

2. Modulus
   The point on the curve which has a tangent based on a slope of 20 lb increase in modulus per minute of cure denotes an optimum cure of 43 minutes.
3. Hardness.
   The point on the curve which has a tangent based on a slope of 0.2° (1/5°) increase in hardness per minute of cure denotes 48 minutes. Hardness is less specific than other constants and because of this is less frequently used.

The optimum cure of such a stock is quoted as 45 mts at 138°C.

The above details on optimum cure are related only to natural rubber and do not apply to SBR in which case hardness and modulus continue to increase beyond the optimum cure point. However this gives an insight into the cure state after all of the vulcanizate in general. Tear resistance and cut growth and permanent set, however, have been used to determine the optimum cure of SBR.

10.6 Control of Production Cures

- Specific gravity which can be easily determined is not strictly a check on cure state but on materials which may affect cure.
- The simplest check on cure is by a hardness determination which is to be done after the vulcanizate is sufficiently cooled to room temperature and the test is done better after 24 hours of cure.
- Reducing scraps which are due to undercure or air trapping.
- Fixing of thermocouple at various locations in the vulcanization equipment and monitoring the temperature of cure accurately.
- Adhesion tests of rubber to metal or rubber to fabric is to be done in counter samples kept along with the products in the curing equipment.

- Chemical analysis of free sulphur provides one of the most generally accepted methods of determining the state of cure and the same is to be done on the compound batch.
- A swelling test indicates the degree of vulcanization.
- Samples can be cut and prepared from the product itself and tests should be conducted on them for tensile strength, modulus and hardness.

10.7 Vulcanization Time

The total time of vulcanization is split into two steps:

1. The time taken to heat the rubber to curing temperature, and
2. The time to cure the rubber after the curing temperature has been attained.

The latter is predetermined and fixed for a given temperature and the former is the time for warming up the stock and can be referred as the warming or preheating time. A shorter curing time does not necessarily mean the use of steam since unit weight of rubber requires a definite quantity of heat. In open cures involving air, the cure time can be reduced considerably by circulating the heating medium as the cold rubber cools the air in direct contact with it and then acts as an insulator. Where saturated steam under pressure is used for curing lined vessels and tanks, the cold rubber surface causes steam to condense at the same time giving up its large content of latent heat. The condensation causes a reduction of pressure, ,attracting more steam at that point of contact.

No one curing process posesses all the virtues and those which may appear to be most desirable may be rejected on grounds of initial cost and maintenance of the equipment. For example even an autoclave curable rubber lined vessel can be cured in open steam at atmospheric pressure and this method can be adopted while the autoclave is down for repairs and maintenance.

10.8 Common Defects in Vulcanizates

Most of the defects in the finished products are attributed to improper mixing of the compound. Assuming that proper mixing has been done, the following product defects can be due to deviations in the conditions prescribed for vulcanization, such as pressure, temperature as well as the process of vulcanization itself. Some of the most commonly occurring defects and their probable causes and remedial measures are given below.

10.8.1 Air Blisters

Air blisters generally occur due to trapped air during the processing of the rubber in the calender or extruder or during hand building up of the products. The remedial measures to be undertaken are: 1) Modify process temperature or pressure, 2) Feed the calender or extruder with adequate rubber stock, 3) Prick out visible blisters when the compound is in unvulcanized state, and 4) Use bleeder cords between metal and the rubber sheets applied at the welded places in the rubber lining process.

10.8.2 Tearing

This is due to over-vulcanization. The remedy is to reduce cure times and temperatures or modify the compound formulation to reduce the speed of cure. Tearing can also be due to method of removal of the product from the mould while it is in hot condition. Tearing can be eliminated by removing the products from the mould after sufficient cooling or by careful and slow removing.

10.8.3 Porosity

Volatile substances in the rubber or compounding ingredients or moisture can cause porosity. Insufficient stock of rubber in the mould and under cure also cause porosity. To prevent this defect from occurring, avoid use of raw materials containing volatile materials, test all raw materials for moisture content, allow the solvents or adhesives to dry up completely, check up the volume and shape of the finished product and increase curing pressure if feasible.

10.8.4 Debonding from Metal

It is often difficult to obtain satisfactory adhesion of rubbers of different compositions and types with metal. The amounts of sulphur and accelerators of various types influence adhesion. These must be chosen so that there is no under or over vulcanization.

To get proper rubber to fabric adhesion the fabric must be quite dry and evenly coated with the adhesive and adequately dried up. Defective adhesion occurs due to contamination by surface blooming of ingredients. Sulphur blooms can be eliminated by the use of insoluble sulphur. Waxy softeners which bloom at the surface should be avoided in compounding formulations.

10.8.5 Surface Scorching

Sometimes the surface of a rubber sheet might have been scorched or pre-vulcanized due to high processing temperatures and storage under improper storage conditions. To avoid this, modify the compound suitably. The preferred temperature for storing the in process stock of rubber can be 20°C to 24°C.

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11

Rubber in Seawater Systems

11.1 Seawater

In many industrial plants such as power generation, petrochemical, desalination, atomic and nuclear power plants and in ships, large quantities of seawater are needed for cooling purposes. This is particularly seen in mid-Eastern countries where other forms of cooling media such as fresh water or air have limited application and seawater is the only readily available cooling medium. The cost of handling a large quantity of seawater is greatly significant, and it is necessary to ensure that the materials that come in contact with this corrosive medium are carefully selected to avoid expensive plant shutdowns. It is important to note that seawater is not a simple solution of inorganic salt in water. It is a complex mixture of many salts, dissolved gases, suspended solids, organic matter and organisms.

Seawater-based utility systems for condenser and process cooling systems in power plants exhibit serious corrosion, erosion and fouling problems. Equipment made from carbon steel and even stainless steel shows sign of degradation from galvanic effect, corrosion, erosion and microbiological induced corrosion (MIC). Corrosion of intake structure and its accessories and process equipment have become an increasing concern due to rising replacement cost of plant equipment, piping materials and impact on system availability. The protection of piping and equipment against seawater corrosion under severe conditions still remains a challenging task. In power plants where seawater is being used, needs have arisen to adopt different corrosion protection measures. These are basically on selection of materials, protective coatings, linings, cathodic protection, control of micro-organism induced corrosion and use of corrosion inhibitors for the equipment such as intake structure, gates and screens; piping, pumps, valves, heat exchangers, strainers, filters etc. Many metallic, concrete and nonmetallic construction materials are used to combat the corrosion prevailing in seawater handling systems amongst which rubber plays an important role as coating and lining. Especially in large size equipment, rubber and ebonite are used on cost consideration apart from their dependability and reliability in preference to steel and other special alloys.

Power plant condenser and process water cooling systems using seawater are normally fabricated from concrete, cast iron, carbon steel, stainless steel, titanium, aluminium alloys or a combination of these along with epoxy or polyurethane coating or rubber lining. Seawater is inherently very corrosive. Plants using seawater as a cooling medium are more severely affected by corrosion. Damage caused by seawater affects the design and economic life of equipment and structure considerably. Hence, they demand special care in the system design and material selection. In a typical power plant, the main components and equipment for seawater-based cooling systems are intake structure, stop log, trash rack, fixed and traveling water screens, intake tunnel piping, self-cleaning filters, heat exchangers, condenser tubes, tube sheet and condenser water boxes. In order to achieve trouble-free operation, it is important for these systems to withstand corrosion, erosion, abrasion, installation impact, mechanical abuse and galvanic effects. The variation of water level at intake also has a great impact on the corrosion of the submerged structure. Thus selection of proper construction material, lining, coating material, fabrication and inspection requirement and installation procedures for each of the seawater-based systems clearly offers one of the most difficult tasks.

As technology developed, many different types of metals and alloys were used to find the best solution. The practice of internal coating of pipes has been used since 1955 on water lines to ensure high purity or to increase the throughput. However, in the later decades this practice has also been applied to process systems based on seawater application to provide enhanced corrosion protection. It is also observed that the pipe internal coating with a polymeric or rubber composition has a significant reduction in deposition of foreign material on the pipe surface. Elimination of the corrosion, abrasion, and galvanic effects on all metal and concrete surfaces can be accomplished using specially formulated rubber lining or cladding material.

11.2 Design Considerations in Seawater Corrosion Protecting System

Seawater as mentioned earlier is mostly the process cooling fluid for coastal based power plants. The main design considerations for selection of corrosion protection measures for seawater-based process cooling systems are:

- Initial construction material.
- Lining or coating requirement.
- Type of corrosion.
- Accessibility from inside and outside of the equipment and piping.

Much effort has been put into finding the proper material for seawater applications. Some of the materials for seawater applications are concrete with or without protective lining, carbon steel with protective lining, stainless steel, titanium, inconel and aluminium alloys.

Stainless steel 316L material used for piping and equipment shows considerable corrosion resistance because of the beneficial effect of molybdenum on the surface properties. It is also observed that the surface treatment (pre-reduced, polished, passivated and chemically treated surfaces) of stainless steel equipment and piping reduces the corrosion process in seawater applications. The corrosion resistance of stainless steel in seawater applications can also be enhanced by bulk alloying the stainless steel with nitrogen, chromium, molybdenum and nickel by converting the stainless steel into super austenitic stainless steel. From leaching studies it is also observed that the release of iron, chromium and nickel from the super austenitic stainless steel to seawater is considerably less than that of stainless steel grade 316L. Titanium has high resistance to various forms of corrosion, however it may suffer hydrogen embrittlement under cathodic protection if applied potential is more negative than a threshold limit.

Coating technology has originated from coal tar enamel to epoxy and polyurethane. The conventional thin-film coatings cannot provide long-term protection on different design considerations such as corrosion, abrasion, and galvanic effects on all metal and concrete surfaces. The longevity of these coatings is affected by formulation of coating, degree of surface preparation, application and application conditions and the severity and type of working environment. Development of new products based on different chemistries along with improved techniques and processes in relation to surface preparation, application, inspection methods and type of equipment have enabled coatings suppliers to enhance the service life of the coating systems.

The high performance coating, such as glass flake filled coatings, solvent-less epoxy, solvent- less elastomeric polyurethane, epoxies, surface tolerant coatings and antifouling coating have been developed in the last two decades for application in marine environments. Salient selection criteria for coating generally adopted for use in process piping and equipment are:

- Chemical compatibility with the operating system.
- Chemical compatibility based on environmental limitations on emissions.
- Adhesion to all substrates.
- Resistance to galvanic potentials in use.
- Easy application and repair by hand or with conventional spray equipment.
- Requirement on surface preparation.
- Ambient or low temperature curing capability.
- Moisture tolerance or ability to cure underwater.
- Abrasion resistance.
- Flammability potential.
- High performance with minimum number of coats (one or two coats).
- Ability to withstand both normal temperatures and occasional temperature fluctuations.
- Resistance to scale and algae formation and easy to clean.
- Life for long term protection.

The lining or coating design should take care at the junction point or at transition points of the equipment and pipe fittings which are more vulnerable to corrosion than the general surface of the pipeline. Presently anti-fouling conductive coatings are also being used in sea water based marine structures and equipment to avoid marine organism growth and adherence to the underwater surfaces. The water in the coating may cause swelling of coating, leading to the degradation of coating. In addition, water affects the permeation of oxygen and other corrosive agents, and consequently the presence of such substances at coating-metal interface promotes corrosion of metal substrate.

11.3 Epoxy Resin

Epoxy resins have application as protective coatings in the engineering field because of good performance, durability and ease of application and a variety of other properties such as chemical resistance, dielectric constant, insulating properties, low shrinkage on cure, dimensional and thermal stability, adhesion, bacterial and fungal resistance. In the cooling water system, the epoxies are chosen for mild chemical and abrasion (sand, silt) resistance and have a hard smooth finish when cured. Some of the flexible epoxy products such as epoxidized rubbers have a rubber molecule built into the epoxy resin molecule, which results in a stable product with excellent flexibility and a high level of abrasion resistance. The flexible epoxy has good performance for condenser water boxes and circulating water system equipment and lines. Patching up of existing lining can be done relatively fast with the coupling of fast reacting hardener with a fast reacting resin to functionally cure the lining.

11.4 Elastomeric Polyurethane Coating

Polyurethane coatings are being used for the industrial application as corrosion protection measure on surfaces as a primer or final coating. The coatings/formulations made of polyurethane materials offer good performance and corrosion protection for seawater applications. Presently 100% solids, solvent less, elastomeric polyurethane is being used as coating due to its large film-build, formation of a monolithic membrane, flexibility, elongation, good adhesion and impact and abrasion resistance.

11.5 Surface Preparation Methods

As the epoxy/substrate bond is mechanical, not chemical, it is absolutely necessary that the surface be clean, dry, oil-free, and have a recommended surface profile. Surface preparation is one of the most important factors in performance of any coating. It includes:

- Pre-cleaning to remove surface contaminants.
- Cleaning of the surface to the desired level.
- Producing a profile for good adhesion.

The coating failures are generally related to poor surface preparation. The poor surface preparation can result in inadequate bonding of coating or blistering and thus shortens the coating system life. Strong adhesion is important for coating performance and long life. Adhesion behavior can be severely affected by the presence of impurities including rust, moisture, mill scale, salt and other particles, grease and oil, dirt and dust, soluble salts and chemicals, water, moisture and loose cracked or peeling paint. Controlling the environmental conditions surrounding the steel surface during surface preparation and coating is fundamental and important to improving coating adhesion, thereby enhancing the performance and reliability of protective coatings. Following are some of the recommended removal methods for different contaminants:

Cleaning method	**Contaminants**
Degreasing	Grease and oils
Power washing	Dirt
Hand and power tools	Loose rust, mill scale, loose paint
Low pressure water cleaning	Dirt
High pressure water jetting	Marine fouling, loose rust and paint
Ultra high pressure water jetting	Rust, tight paint
Abrasive blasting	Rust, Mill Scale, tight paint

Cathodic protection is an electrical means of eliminating corrosion in pipelines, where corrosion occurs, and corroding current flows from pipelines into the surrounding electrolyte (soil or water). Likewise, at cathodic areas the current flows from the electrolyte onto the pipeline, and pipe does not corrode. If every bit of exposed metal on the surface of a pipeline could be made to collect current, it would not corrode, as the entire surface would be cathodic. Direct current is forced to flow from a source external to the pipeline onto all surfaces of pipelines.

11.6 Specific Corrosion Protection Measures

To obtain longer service life from power utility condenser and process water cooling systems, better materials and maintenance procedures is the need of the hour. In an effort to increase the abrasion resistance, rubber lining is used for piping and structures in seawater systems. The rubber, while solving the problems of erosion and corrosion, is susceptible to outside damage from debris or during outages, from workers. However, it is still used for lining if isolation for maintenance and replacement is available, as well developed technology for this is available at cheaper cost. As the rubber lining ages, problems with adhesion sometimes lead to failures of large sections coming out and plugging the equipment. One of the earliest organic linings used for circulating water systems was coal tar epoxies. The original formulations were solvent based but nowadays 100% solid based products are available.

Algae, clams, mussels (biological organisms) etc., all can cause severe problems in the circulating water system. Algae mostly cause loss of flow and can add to the energy required to pump the cooling water through the system. Clams and mussels can attach to all surfaces and grow to a size large enough that when they die or are killed, they release from the wall and can be carried to blocking the opening (specially with heat exchangers/condensers), thereby restricting the amount of cooling available.

In Indian nuclear power plants, chlorination is being done, with proper control on discharge limits, in seawater systems to control biological fouling. Systems are being developed for use of chlorine-dioxide in place of chlorine for better efficiency to control the growth of algae, clams, and mussels. Non-toxic, non-polluting means for eliminating the growth of algae, clams, mussels, etc. in seawater systems are also being used. One approach is the use of a silicon - based product, which gives a non-adherent surface and which does not allow the larva to attach and grow; rather they are washed through the system. These products require a smooth surface for best performance and must be applied onto a base of epoxy.

11.7 Intake Water Tunnels

Intake water tunnels are generally made from concrete, and absorption of water by concrete is the main reason for corrosion in reinforcement. In intake structures the problems are due to concrete failure from salts penetrating into the concrete and corroding the rebar. Hard, dense concrete with ample cover to reinforcement and without cracks and porosity has good resistance to corrosion against seawater. In Indian nuclear power plants, the experience with concrete intake tunnels with respect to corrosion behavior is not bad except that special care is required for protection against algae, clams, mussels, etc. which attach to the tunnel surface.

The coating system adopted for these structures must be moisture tolerant and be able to cure at or below ambient conditions. In some cases material may have to be used in wet surfaces because of the inability of getting the surface completely dry. The rubberized epoxy copolymer is suitable for such application. For concrete tunnel repair, the damaged concrete must be removed to expose undamaged rebar. The rebar are repaired with proper coating after cleaning by grit blasting and the concrete is to be rebuilt with epoxy.

11.8 Trash Rack and Traveling Water Screens

Traveling water screens were usually made in the past from carbon steel and are generally painted with coal tar epoxy. Stainless steel wire is used for screens and the carbon steel structural part is coated with anticorrosive polymeric or rubber coatings. The carbon steel structure becomes increasingly susceptible to general and galvanic corrosion once the original coating has deteriorated. It is difficult to perform repair work properly in the field because of the problem with surface preparation. The traveling screens are usually removed for replacement. This increases the cost and makes the selection of long lasting (30 to 35 years) coating systems necessary. The coating of carbon steel frame, if the screens are made of stainless steel, must be able to resist the galvanic potential bond to stainless as well as carbon steel, and should have enough abrasion resistance to handle the movement of the screen. In Indian nuclear power plants coal tar epoxy was initially used and later replaced with stainless steel 316 materials with moderate to good experience. Trash screens are usually coated for abrasion resistance and also for resistance to galvanic effects with a suitable polymeric material. Trash rack is also made from stainless steel 316 material. The two coastal based nuclear power stations in India, Tarapur Atomic Power Station (TAPS) and Madras Atomic Power Station (MAPS), which use seawater for condenser cooling and process water cooling, have seen seasonal influx of debris originating from marine organism/seaweeds and jellyfish; damage and chocking of the screen was reduced with the use of an extra graded screening system and increased monitoring frequency.

11.9 Condenser Water Boxes

In one of the Indian nuclear power plants some of the condenser water boxes lined with fiber glass epoxy got damaged during the initial operation period. The reason found was improper surface finish and transit damage. The water boxes face abrasion due to water jets, hence the coating should have a good abrasion and chemical resistance and rubberized epoxy copolymer lining is suitable. Water boxes protected in this manner can have an expected life of twenty to thirty years. Cathodic protection is generally provided in condenser water boxes and the cathodic protection current requirement reduces with the use of coating.

11.10 Condenser Tubes and Tube Sheets

Condenser tube sheets suffer from virtually all forms of attack, galvanic corrosion, chemical corrosion, crevice corrosion, microbiologically induced corrosion and erosion. In Tarapur Atomic Power Station in India condenser tube failure was observed in the initial operating period and this problem was resolved by providing 150 mm long plastic inserts in the tubes and involving periodic cleaning of tubes and water boxes , maintaining epoxy lining along with anodic protection. Titanium tubes and titanium clad tube sheet for condensers gives long-term trouble-free operation.

Based on operating experience titanium condenser tube along with titanium clad tube sheet have been used for the Tarapur Atomic Power plant.

11.11 Piping, Pumps and Heat Exchangers

In the initial design of the seawater intake pumps the commonly used material for impeller was zinc free bronze and Al-bronze with 5% Ni. Corrosion problems, however, occurred with these materials in the Indian plant. It is apparent that the initial selection of better material for components in critical areas would considerably reduce future operational problems and provide long life.

11.12 Field Observations

During installation and field welding, special care is needed at the junction point of the equipment and pipe fitting or at transition points between pipe and fitting which are more vulnerable to corrosion. The reason for this is either change in material properties, presence of defects, change in flow pattern causing erosion, or difficulty in providing proper protection measures due to restricted approach and size. Requirements of different mechanical and chemical properties of lining/coating at transition points of equipment and fitting needs different lining/coating material, hence joining two different lining and coating materials needs special care during construction. One of the problem areas is the junction point between concrete lined pipe and rubber lined flange, which needs special joint design to reduce the chances of lining failure. In nuclear power plants stainless steel 316L material is used for small size pipes. In process systems the piping, valves, equipment and fittings used are of various sizes and types and there are more field joints. Therefore, the success of the lining/coating system depends on its suitability for field and in-situ application. During field welding of large size concrete lined pipes, it was observed that, to avoid cracks in the concrete lining during field welding of large size concrete lined pipes, minimum 250 mm long unlined portion of pipe is to be kept at the end for welding. This bare portion is to be lined with concrete after completion of the weld inspection. It is difficult to qualify a lining at the small branch connection less than 25 mm in size used for instrument connection; in such cases the branch connection shall be larger than 50 mm size with flange connection for installation of small size instrument connections. In some piping spools where large numbers of branch connections are needed for equipment for instrumentation, the design provision is to be made for repair/replacement of such lined spool pieces, as this is the most likely area for lining failure.

The primary objective of protective coatings is to prevent corrosion of the substrate. Unfortunately, premature coating failure is often due to either incorrect coating application and surface preparation, or an inherent weakness in the coating formulation. The quality assurance on the performance of protective coating is to concentrate on the long term properties of the coating or coating system, and how it performs under various aggressive conditions seen during service life. Generally, all the paint companies have their own methods for testing coatings. The durability and quality of sophisticated coating systems depend on inspection requirements. These are visual inspection, instrumental test, surface preparation inspection, dry film thickness measurement, coating flow detection (Holiday detector), adhesion testing. There is no perfect everlasting coating for all conditions. However the protective coating systems which carry approvals with quality inspection and testing can qualify performance requirements.

Much work has been done on development of qualification procedures, test methods and acceptance criteria for pipeline coating. Some of the requirements to control the quality of the coating are on wet film thickness measurements and surface profile readings on large jobs. These data are taken at regular distance as determined by supplier/user and the readings recorded for future use. Humidity; air, surface, and coating temperatures are very important and are also measured and recorded during coating. For large areas the water dew point is to be controlled using either dehumidification or heating the substrate to at least 2°C to 5°C above the dew point or both. To avoid bonding problems it is necessary to prevent rust and ensure that the substrate is clear of any moisture film.

Major causes for coating failure are surface cracking and undetected pinholes or voids. These can be repaired and serious problems avoided. Coatings generally fail in different modes, these are: chemical failure, abrasion failure, adhesive failure, cohesive failure and undercoat corrosion. For performance evaluation of coatings on experimental basis on these parameters various ASTM and BS specifications are presently being used.

It can be concluded that selection of proper material or lining for seawater application is important and depends on the criticality of the system, availability of standby system/equipment and availability of isolation devices for maintenance. For process piping in seawater application the success of proper lining or coating material depends on the suitability for in-situ/field application and the proper corrosion monitoring plan.

11.13 Material of Construction for Seawater Based Systems in Nuclear Power Plants[1]

Large and medium size piping and valves require rubber or rubber lined construction whereas smaller ones are constructed with mild steel, concrete or stainless steel of suitable grade.

Condenser and Process Cooling Water System

Piping:

2000mm NB to 2500mm NB – Mild steel, internally lined rubber.
≤ 150mm NB - SS 316L
>200 NB to 900 NB – Mild steel, internally rubber lined
1000 NB - Mild steel, internally lined with 25 mm thick concrete mortar and externally lined with 25 mm thick gunitting

Buried pipes: Externally lined with protective tapes and coating with epoxy:

Large sizes: Concrete tunnel with coated reinforcement bar.

Valves:

Higher size: Ebonite lining.
Medium Size: EPDM lining.
150 NB and smaller size: SS 316 material

Pump House Forebay:

Concrete structure: constructed with coated reinforcement with polyurethane coating on surface.

Stop log:

Carbon steel with polyurethane coating.
Screens frame: carbon steel with polyurethane coatings.

Screen and trash rack: SS 316
Screen support structure (under water): S.S.316
Screen support structure (above water): Carbon steel with polyurethane coating.

Reference

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12

Rubber in Oil Field Equipment

In the oil field industry fluids such as well fluids, completion fluids and stimulation fluids [1,2,3] are used. It would be meaningful to know about these fluids and their corrosive characteristics since they have an adverse effect on rubber components such as packings, gaskets and seals exposed to such environment. The details of these fluids are given below.

12.1 Well Fluid

When drilling or completing wells in earth formations, various fluids typically are used in the well for a variety of reasons. The fluid often is water-based. Such fluid is referred to as "well fluid." Common uses for well fluids include: lubrication and cooling of drill bit cutting surfaces while drilling, controlling formation of fluid pressure to prevent blowouts, maintaining well stability, suspending solids in the well, minimizing fluid loss into and stabilizing the formation through which the well is being drilled, fracturing the formation in the vicinity of the well, displacing the fluid within the well with another fluid, cleaning the well, testing the well, abandoning the well or preparing the well for abandonment.

12.2 Completion Fluid

Completion fluids improve well productivity by reducing damage to the producing zone, and they can help prepare, repair, clean out and complete the well bore during the completion phase. Completion fluid is a solids-free liquid used to "complete" an oil or gas well. Completion fluids are typically brines (chlorides, bromides and formates), but in theory could be any fluid of proper density and flow characteristics. The fluid should be chemically compatible with the reservoir formation and fluids, and is typically filtered to a high degree to avoid introducing solids to the near-wellbore area. Seldom is a regular drilling fluid suitable for completion operations due to its solids content, pH and ionic composition. Drill-in fluids can, in some cases, be suitable for both purposes.

12.3 Stimulation Fluid

Stimulation fluid is a treatment fluid prepared for stimulation purposes, although the term most commonly is applied to matrix stimulation fluids. Most matrix stimulation fluids are acid or solvent-based, with hydrochloric acid being the most common base due to its reaction characteristics and its relative ease of control. Matrix stimulation is a process of injecting a fluid into the formation, either an acid or solvent at pressures below the fracturing pressure, to improve the production or injection flow capacity of a well.

In such oil field environments, the situation is more complex for the rubber material either a seal or any other component because of the following reasons.

- During the oil field operations, the combinations of carbon dioxide and hydrogen sulphide with or without water creates aqueous and non-aqueous electrolytes.
- The gas concentration (partial pressure) at temperatures above critical can act as a super critical solvent. Rubbers in this environment are subjected to high swells leading to subsequent extraction of plasticizers, low molecular weight polymers etc.
- Explosive decompression in the oil field operating conditions due to pressure or temperature shifts can cause catastrophic seal rupture.

- The inevitable introduction of acids such as hydrochloric, hydrofluoric, bases, metallic halides, carbonates and gases like carbon dioxide and nitrogen create another set of problems for the seal. The oil field duty condition is very critical and unique, and therefore there is very little technology transfer potential.

The problems encountered by rubber technologists in designing compounds for oil field duty conditions are as follows:

- Differences in the types of carbon black used in the oil field service lead to the seal explosive decompression problems. The molecular weight of the base rubber also is very critical.
- Conventional materials like different metal oxides are used in the curing systems of the rubber compounds. When used, these are freely present in the compound, soluble in the inorganic acids that are used in the oil exploration industry and lead to high swelling effects on rubber.
- If non-black fillers are used they produce excessive swelling and softening of the rubber sealing rings in the aqueous medium, where oxides become hydroxides and silicates are converted to water soluble bicarbonates by carbon dioxide and water.
- Rubber degradation in the sealing system occurs when in contact with high pH (basic) and low pH (acidic) fluids in the systems.

If the above is taken into consideration one would understand pretty well that typical oil field rubber compounds are very difficult to process as they have to be based on high molecular weight rubbers and highly reinforcing fillers. But unfortunately such compounds will obviously have undesirable higher compression set values because of the use of high reinforcing fillers and compounding ingredients which are necessary for the oil field fluid resistant and leakage prevention requirements.

A most dominating chemist as well as a chemical engineer or a corrosion engineer who is involved in the oil field industry will certainly appreciate the fact that rubber is an engineering material. In an engineering sense, molded rubber components are used under strain and stress. Compounding for each of these categories can have considerably different approaches. The following three basic factors are considered while designing compound formulations for stress or strain:

Rubbers or elastomers;
Fillers;
Cross link agents.

Rubber can be considered as a thermodynamic system, the first law explaining quantitatively the property of elasticity and the third law illustrating the thermal pressure created in the molding process. The ideal gas law, PV = nRT is in evidence since the application of rubber components by nature are subjected to changes in temperature. In the consideration of molecular weight of a rubber or high polymer, one has to remember that more repeating units or a number of monomeric units constitute a typical polymer chain. The lower the molecular weight, the lower is the mooney viscosity can be considered as a rule-of-thumb. Low die-swell indicates low molecular weight. Narrow molecular weight distribution of high molecular weight rubbers have better characteristics in molding. A perfect rubber selection for a sealing device in the corrosive environment in the oil field industry is very difficult since dynamic duty conditions prevail here.

Fillers have numerous functions in a rubber compound. But common to all is their effect brought about by increasing the viscosity of the formulations. For more rigorous oil field sealing application, particularly the downhole operations, the preferred filler is carbon black. Since the oil field production environments involve methane (CH4), hydrogen sulphide (H2S) and carbon dioxide (CO2) gases coupled with low as well as high pH value acids and bases non-black fillers can create additional potentially serious complications. There is a strong possibility of a vigorous attack by such operating conditions in an oil field industry on the reinforcement of rubber.

12.4 Explosive Decompression

The reinforcing effects of fillers cannot be overlooked while keenly keeping in mind the essential performance requirements of a rubber sealing ring for oil field service. Briscoe and Zakaria et al. [4] in one of their many papers gave additional insight into the carbon filler- rubber adhesion during reinforcement. They observed that the degree of adhesion of a filler in a rubber influence the carbon dioxide gas sorption as indicated below.

Table 12.1 Filler/Gas uptake relationship

Condition	**Percent gas uptake %**
No filler	133
Untreated filler-20%by volume	145
Coated filler-20%by volume	150
Filler Silane coated-29%by volume	120

From the above table it is seen that the coated filler accommodates more carbon dioxide leading to blistering in the seal, which is known as explosive decompression. It becomes evident that rubber compounds that have low permeation rates are chemically resisting the permeation of gases and are the best to minimize blistering due to the cavity or vacuoles in the rubber or polymer matrix.

The following table 12.2 [5] shows the effects of four important filler variables on the physical properties of a sealing compound,

Table 12.2 Effects of filler

	Increasing quantity	**Increasing surface area**	**Increasing structure**	**Increasing surface reactivity**
Hardness	↑	↑	↑	↑
Dynamic modulus	↑	↑	↑	↑
Static modulus	↑	↑	↑	↑
Tensile strength	↘	↑	↔	↔
Elongation	↓	↔	↓	↘
Compression set	↑	↑	↑	↓
Tear strength	↘	↑	↔	↑
Fatigue life	↘	↓	↑	↑
Abrasion resistance	↘	↑	↑	↑
Impact strength	↘	↑	↑	↑
Heat buildup due to hysteresis	↑	↑	↓	↓

Table 12.2 (cont.) Effects of filler

	Increasing quantity	**Increasing surface area**	**Increasing structure**	**Increasing surface reactivity**
Extrusion resistance	↑	↑	↑	↑
Blister resistance	↑	↑	↑	↑
Electrical conductivity	↑	↑	↑	↔
Processing				
Incorporation time	↑	↓	↑	
Dispersibility rating	↔	↓	↑	
Mooney viscosity	↑	↑	↑	
Extrusion die swell	↓	↓ Slightly ↓		
Key ↑ Increases ↓ Decreases ↔ No significant change ↘ Goes through a maximum				

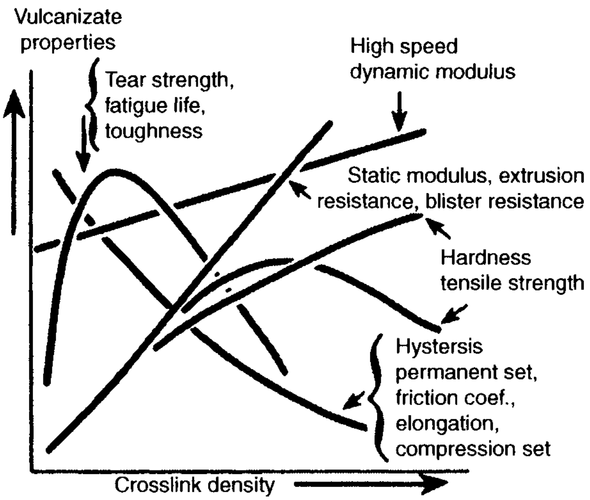

Figure 12.1 Vulcanizate properties vs crosslink density.

those being quantity, surface area, structure and surface reactivity. The resistance to blistering or explosive decompression is found to be increasing with increase of all four variables. One could see the trend from this table in the change of properties listed with an increase in each of these variables. This table should be studied in conjunction with the above figure 12.1, from which the specific properties can be optimized. Since each of these variables can affect properties differently, and cross link density of the compound also can affect properties in a different manner as shown in the figure, the choice of properties that must be optimized should be selected very carefully and should be limited.

The function of cross link requires no elaborative discussions in the matter of product design since the implications of the same on the physical properties are quite obviously mentioned in many textual treatises on cross linking of rubbers. The cross link density directly affects physical properties such as heat build up, tear strength and elongation, too.

12.5 Effect of Increasing Molecular Weight

In the case of amorphous rubbers the effect of increased molecular weight on their physical properties deserves careful consideration. The following table 12.3, lists many of the properties which improve as the molecular weight increases. The enhancement of rubber properties with increased molecular weight has been known for many years, but because of the difficulty of processing these high molecular weight rubbers into functional products has been limited. However for high pressure and high temperature sealing applications as in oil field service only high molecular weight rubbers are suitable since they possess low compression set along with other desirable functional properties.

A careful study of the above tables and figure 12.1 will indicate why a rubber chemist spends a lot of time in designing compounds with various cross link densities for oil field service as well as for other critical applications. It can also be observed that tear strength, fatigue life and toughness, all important requirements for oil field, rubber seals pass through an optimum at low cross link density and fall off with increase in cross link, whereas the most important sealing properties such as hysteresis and compression set improve with increased cross link.

Table 12.3 Effect of increasing molecular weight

	Increasing molecular weight
Hardness	→
Dynamic modulus	↑ Slightly
Static modulus	↑ Slightly
Tensile strength	↑
Elongation	↑
Compression set	↓ (Improves)
Tear strength	↑
Fatigue life	↑
Abrasion resistance	↑
Impact strength	↑
Heat build up due to hysteresis	↓ (Improves)
Extrusion resistance	↑
Blister resistance	↑
Electrical conductivity	→
Processability	↓
Key ↑ Increases ↓ Decreases → No significant change	

In high pressure sealing in the oil field service, it should be noted that hardness, modulus, extrusion resistance and resistance to blistering under rapid decompression can all be increased with an improvement in cross link density. However the elongation is reduced, the elasticity diminished and so the sealing potential is lessened.

To more completely appreciate the challenges of successful oil field elastomer formulation, a brief review of the operating environment will be useful. Energy production has moved from the relatively benign hydrocarbons to the very complex environment. The benign environment, even if at higher temperatures, was straightforward in the sense that conventional nitrile and fluoroelastomer sealing material technology was adequate and predictable in service life. The complex environment not only occurs naturally but is also developed in low-sulfur wells during secondary recovery by water flooding.

The aggressive environment is more complex for the following reasons:

1. The combinations of CO2 and H2S, with and without water, create aqueous and non-aqueous electrolytes. An understanding of Lewis acid-base interactions is necessary to appreciate the problem potential. (Note: The Lewis acid and Lewis base concept explains the majority of reaction chemistry that we are familiar with. Lewis acid/base reaction chemistry concerns: electron pair donors, electron pair acceptor, anions, cations, lone-pairs etc.) [6,7].
2. Gas concentrations (partial pressures) at temperatures above critical can act as supercritical solvents. Elastomers in this environment are subject to high swells and subsequent extraction of plasticizers, low molecular weight polymers etc.
3. Explosive decompression due to pressure or temperature shifts can cause catastrophic material failure.
4. The deliberate introduction of acids (HCl, HF), bases (inhibitors) completion fluids (metal halides, carbonates etc.) and gases (CO2, N2) creates another set of problems. These interactions are reasonably well understood by only a very few users. The oil field environment is unique and there is no other environment with similar problems; so there is little technology transfer potential.
5. High swell in inorganic acids (acidizing) since conventional technology used different metal oxides in the cure system that are soluble in these acids.
6. Excessive swelling and softening in the aqueous environment if non-black fillers are used (oxides become hydroxides or sols, silicates can convert to water-soluble bicarbonates by carbon dioxide/water mixtures etc.).
7. Rapid seal and gasket material degradation in the presence of high pH (basic) environments such as inhibitors, carbonates (completion fluids).

Oil field users should be aware that the standard commercial rubber compounds incorporate little if any of the specific compounding approaches necessary for successful oil field compounds. This is due to:

1) Typical oil field compounds are more difficult to process (high molecular weight and more reinforcing fillers).
2) Compounds for oil field service typically have higher compression set values due to use of fillers and compounding ingredients dictated by the oil field service requirements.

Elastomers are created from two or four carbon gaseous monomers. The resulting material has increased density which is a thousand fold and the viscosity is 1014 higher than the gaseous state. The elastomer viscosity is sufficiently high that we can measure it in terms of megapascals (MPa), or in engineering terms of Youngs '(E) and shear (G) modulus. It is essentially a super-condensed gas. Rubber is a thermodynamic system, the first law explaining quantitatively the property of elasticity and the third law illustrating the thermal pressure created in the molding process.

When considering molecular weight, one has to remember that a more legitimate value is the constitutional repeating units (CRU) or number of monomeric units creating a typical polymer chain. A low mooney value might be 500–750, medium 1000–1500 and high 2200 and up. Remember also that molecular weight values can be misleading, emulsion-type high mooney elastomers such as SBR and NBR have extensive branching, often creating "gel" or an insoluble residue (due to cross links). What is typically helpful to the molding operator (low viscosity, low die swell etc.) is a disadvantage to the end user, i.e., low viscosity is typically low molecular weight (M.W.) giving reduced mechanical properties. Low die swell usually indicates both low M.W. and high gel. Both are a distinct disadvantage for applications such as packing materials. It is surprising in the study of rheology, that narrow distribution higher molecular elastomers have better flow characteristics than their lower mooney, branched analogs. Die swell is higher for these elastomers, however.

A typical elastomer selection for service in the oil field environment is often based on what might logically be described as the best of a bad lot in the selection process. Elastomers based on addition polymerization reactions,i.e., NBR, FKM, CR, EPDM are more predictable in the aqueous and non-aqueous oil field applications. Ring opening polymerizations (polyphosphazenes, polyalkylene oxides) as well as condensation reaction polymerization (AU and EU) are very vulnerable to acid - base environments and caution is urged when they are utilized.

Fillers serve numerous functions but common to all events is their effect brought about by increasing the viscosity of the formulation. There is the strong possibility of a vigorous attack by the operating environment on what is basically the reinforcing mechanism of the elastomer in highly loaded compounds. The function of cross links requires no elaboration. How they are created and how they subsequently perform is another story told in chapter 10.

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13

Calendering of Rubber and Coated Rubber Sheets

13.1 Calendering Machine

Rubber sheets are the most important materials for the construction and fabrication of much chemical plant equipment such as storage tanks, reactor vessels, pipelines, seals, hoses and rubber lined mild steel equipment of different sizes and shapes, inflatables, etc., and almost all equipment subjected to different corrosive environments. The rubber sheets can be either plain or fabrics coated with rubber. The fabrics used for coating are nylon, rayon, cotton or various other synthetics. Rubberized fabric cords are also used as reinforcing members in various products.

In the production of fine rubber sheets or coated rubber sheets, the main equipment used is a calendering machine. Though rubber extruding machines which are later developments are used for manufacturing some sheet profiles, the calendering machines are the ones used widely in the rubber industry for the manufacture of rubber and coated rubber sheets. Calenders are conveniently used for the continuous production of rubber sheets from different types of rubbers.

In the rubber industry, apart from the mixing mill, the two major processing machines are calender and extruder. These machines have to be fed with a warmed stock of rubber from mixing mills which are operated either alone or in train. The extruder is widely used to extrude tubes and profiles of different cross sections.

There is little work of a fundamental nature done that helps towards a better understanding or control of calendering of rubber. Most theoretical studies were concerned with the pressure developed when a stock of thick viscous rubber sheet material is reduced to a thinner sheet by passage between rolls. Calenders with 3, 4 or more rolls might be assembled to quite different configurations. Calenders in L shaped, F shaped, I shaped or Z shaped configurations with roll diameters of 168 mm, 250 mm and 350 mm are available on the market.

The calendering machine of three, four or more hollow rolls has arrangements for heating by steam or hot water or cooling by refrigerated water. The widths of the calender rolls may be only six inches for a laboratory size calendering machine or up to hundred inches when heavy work and a large volume production are required.

13.2 Calender Design Features

Taking the example of a three-roll calendering machine, the successful calendering operation is ensured by the following basic features.

Rolls
The rolls should be of close grained chilled cast iron. The surface of the rolls must be ground to a perfectly true diameter free from pinholes and should be highly polished to assist the production of first quality defect- free sheeting with a high degree of surface finish.

The frames
The frames of the machine should be sturdy and made of closely grained cast iron of heavy design, free of blowholes which usually form during casting, to withstand the load exerted by the rubber stock.

Roll adjustment
The top and the bottom rolls should be adjustable to keep the nip distance for taking out sheets of precise and uniform thickness. The central roll is fixed.

Roll contours

Theoretically speaking, all calender rolls are true cylinders and as such it will be expected that when they are mounted on the sides of the frames they become equivalent to cylindrical beams supported by bearing blocks at each end and therefore subject to deflection. In addition to this, when the machine is loaded with the pre-warmed rubber stock, the squeezing and the rolling action performed on the stock produce loads which cause further deflection of appreciable magnitude. To counteract this deflection, suitable roll contours have to be provided on the rolls to produce sheets of uniform thickness. A three-roll calender with roll contours exaggerated is shown in the following figure 13.1.

When the rubber stock is passed through the rolls, the pressure between them causes deflection which results in parallel openings or nips between the rolls as shown in figure 13.2.

The contouring of the calender rolls by grinding in order to counteract the natural deflection and the deflection set up by the work being done with rubber stock load is a precision job and in most cases it is done by trial and error method. The nip pressure per inch width of the roll for most rubber compounds has been extensively studied by scientists in the Dunlop Rubber Company [ref: Paper "Estimation of the shear deformation exerted by a roll-mill upon a rubber compound" by T.S. Ng, G. Angerer, Dunlop Forschung, Dunlop-Strasse 2, Hanau, Federal Republic of Germany, Presented at the Jahrestagung der

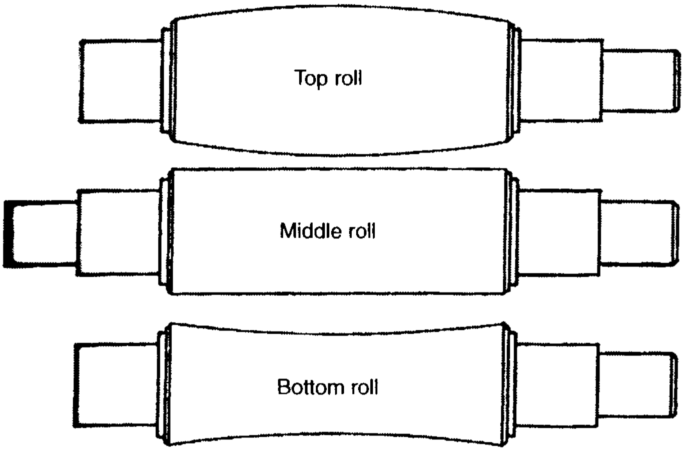

Figure 13.1 Roll contours-calender empty.

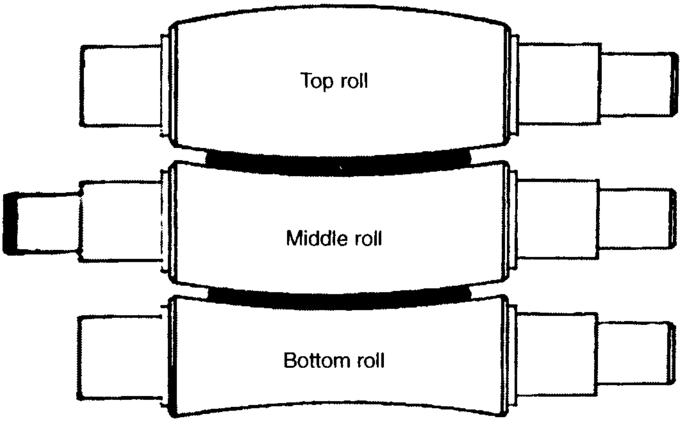

Figure 13.2 Roll contours–calender loaded.

Deutschen Rheologischen Gesellschaft with Conference Chemical Engineering Rheology in Aachen, 5–7 March 1979, ref: Polymer Engineering and Science, Volume 20, Issue 8, Pages 585 - 588, 1980 Society of Plastics Engineers, Inc]. As per sources in Dunlop Rubber Company the nip pressure is of the order of 1500 lb per inch width of the roll for most rubber compounds.

According to a paper by G. Ardichvili at the International Rubber Conference Paris [ref: "Essai de la Determination Rationelle du Bondage des cylinders de calenders" Congress International du cautchouc Paris 1937] the nip pressure is greatest where the thickness is 1.3 times the nip distance. It is obvious, therefore, that a heavy load is encountered during calendering of rubber compounds which causes deflection of the rolls and as such contouring or cambering, as it is sometimes called, of the rolls is very important in manufacturing calendered sheets.

13.3 Fabric Coating-Topping

The introduction of rayon, nylon and other manmade fibers with their greater strengths per unit cross sectional area compared with cotton fabric has led to the use of rubber coated fabrics in the manufacture of various engineering products such as tyres, beltings and hoses and also several specialty products for the chemical process industries. The arduous service conditions prevailing

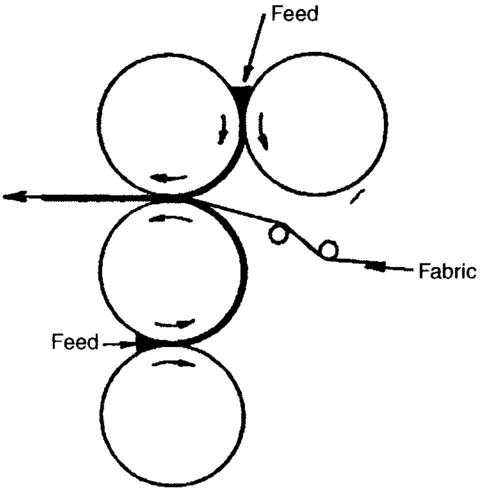

Figure 13.3 Topping on both sides on a four-roll calender.

in the process industries necessitated numerous compounding challenges which resulted in un-vulcanized stock of different mooney viscosities involving different kinds of rubbers. This has made the different calendering operations such as sheeting, frictioning and topping or skim coating of fabrics more critical.

Topping or skim coating is a more attractive and straightforward process when compared with frictioning. Moreover, with the introduction of synthetic and other manmade fabrics it has become essential to apply an adhesive coating generally of the base material of treated latex rubber to the fabric in order to obtain an adequate adhesion in both un-vulcanized and vulcanized sheets. This kind of intermediate treatment has been extended to cotton fabrics, also making the frictioning process superfluous except for closely woven fabrics where a deep penetration is necessary. It has also been employed where a high degree of intimate uncured bond is required to prevent the sheet layer lifting during subsequent operations. For a continuous process of topping simultaneously on both sides of a fabric, a four roll calender is employed as shown in the above figure 13.3.

In setting up the three-roll calender for topping one side of the fabric even surface speeds of rolls are used for the pair of rolls forming the fabric nip and a friction ratio of 3:2 between those forming the rubber nip.

13.4 Frictioning

Frictioning is confined to three-roll calenders operating with a middle roll surface speed of 3:2 for the outer pair of rolls. In the frictioning process the rubber stock called the friction compound adheres well to the middle roll and does not break away under the shearing action occurring in the fabric nip. It is therefore necessary to have a compound with lower carbon black loading and a higher softener content than is considered for a topping compound. Example of a friction compound formulation is given below.

Rubber	- 72 parts
Sulphur	- 2–4 parts
Accelerator	- 0.6 parts
Softener including stearic acid	- 10 parts
Zinc oxide	- 3 parts
Carbon black	- 12 parts
Total	- 100 parts

The roll temperature to be maintained will depend on the processing characteristics of the compound such as mooney viscosity and scorch time. The middle roll temperature should be kept as low as possible generally at 20°C to 30°C lower than the top and bottom rolls since a rubber band of approximately 1.2 mm thickness circulates around the middle roll during frictioning. The cushioning effect of this rubber layer and the fact that the processing merely fills the gaps in the fabric being treated makes the roll contouring less critical than in topping where a fine thinner layer of sheet of rubber with uniform thickness is required to be plied on to the fabric.

13.5 Rubber Sheets

In the manufacture of fine rubber sheets, two essential qualities are required in the finished products, namely, uniformity of texture and even thickness. When sheets of only a few thousandths of an inch thick are required, great care must be taken to ensure this result. The first essential quality is achieved in an adjusted calender with all its bearings in good condition. The rolls must be correctly cambered (grinding to fine convex or concave curves) to give a uniform sheet and the condition of the roll surface must be of the highest order. Any scars or marks on the rolls caused due to passage of small metal objects such as nails, screws or broken knife bits cannot be tolerated. These defects, however, are not very often important for thicker sheets. But in the case of fine thinner sheets, the surfaces must be perfectly free of such defects. An electromagnetic detector might be helpful to eliminate these metallic objects from the compounded stock.

The second essential quality is achieved by a homogeneously compounded stock of rubber. The compound stock might be of low or high rubber content. Mostly a high rubber-content stock of say 50 to 60% is deployed in the manufacture of construction material for process industries and other critical engineering application. The choice of compounding ingredients is usually limited by the exacting demands arising from limits of physical properties of the vulcanizates. The mooney viscosity must be carefully controlled and the warming up process in the mill for calendering must be arranged during production runs to give a constant and continuous feed of uniform mass of compound to the calender. The warming mills and strip feed to the calender must be capable of providing these conditions and for best results the feed should be rapid in a fine and uniform strip of stock.

The rubber bank on the nip of the rolls should be kept small and should roll continuously. It should not be allowed to become large as air blisters will form and the stock will cool and harden leading to sheets of rough surface and varying thickness. The rolls are run at even speed or at a low friction ratio. Sheets that are too thick, say more than 4 mm thick, should not be calendered in one single ply. The most successful and universally followed practice is taking sheets of 1 mm thick and plying them to the required thickness in a doubling device. In this way the pinholes possibly formed in thin single ply sheets can be covered with subsequent plies in the doubling device. Strict control of temperature of the rolls and the nip adjustments are necessary during the calendering operation. For the control of roll temperature a continuously reading contact pyrometer is most suitable. Hot water continuously circulating through the rolls is preferable to steam because it is easier to control. The sheets thus taken from the bottom roll of the calender are drawn through a conveyer belt and wound on rolls backed by a cloth liner.

13.6 The Art of Calendering

The ease with which a compound can be calendered is largely governed by the carbon black loading in the rubber compound and the rubber content and scorch time. Examples of two typical topping compounds are given below.

		A	B
Rubber	-	75 parts	63 parts
Sulphur	-	2 parts	2 parts
Accelerator	-	0.5 parts	0.5 parts
Softeners	-	3.5 parts	6.5 parts
Zinc oxide	-	4 parts	3 parts
Carbon black	-	15 parts	25 parts
Total		100 parts	100 parts

Assuming identical mixing of the compounds, compound B, which contains 10% more carbon black would undoubtedly prove more difficult to calender due to its high mooney viscosity and the resultant higher temperature build-up during calendering. One is therefore dependent upon those steps which the rubber chemist takes, without impairing the ultimate physical properties, to minimize scorching and produce the right compound surface conditions for subsequent handling of the calendered products. It will be noted from the formula that in compound B the softener content has been increased by an additional 30%, thus increasing the plasticity or in other words decreasing the mooney viscosity of the compound and thereby minimizing the scorching tendency of the stock. If calendering difficulties are still encountered, the choice of action lies between either accelerator reduction in the compound formula or increased mastication time as follows:

1. Reduction of up to 10% of the accelerator content may be permissible without seriously affecting the physical properties of the product. This will increase the mooney scorch time by as much as 4 units which is a safe condition.
2. An increase of the mastication time for the uncompounded raw rubber will give an increased margin of safety.

It is not possible to standardise operating temperatures for calender rolls. Although on each calender a set of conditions can be established for several runnings, this may vary approximately on calenders using different types of compounds. It is however a normal practice to operate with lower temperatures for those rolls around which the rubber bands rotate.

Suggested temperatures of the rolls for calendering:

Three-roll calender:

Top roll	-	110°C
Middle roll	-	85°C
Bottom roll	-	cool

Four-roll calender:

Breast roll	-	115°C	130°C
Top roll	-	90°C	100°C
Middle roll	-	95°C	110°C
Bottom roll	-	115°C	130°C

It is desirable to operate with the lowest roll temperatures for achieving satisfactory results. The high temperatures quoted in the second example for the four-roll calender are necessary in those cases where there is a tendency for air trapping between the rubber layer and roll surface resulting in bubbles forming at the fabric nip and disturbance of the fabric spacing. The resultant plasticisation of the compound at the higher temperatures reduces the green strength of the rubber layer and the trapped air breaks through it before the bubbles become large enough to affect the texture of the sheet.

The following factors have a direct bearing on the uniformity of the calendered products such as sheet, topped or frictioned fabrics.

- Prewarming of the compounded stock.
- Feed arrangement – manual or conveyer feeds.
- The presentation of the fabrics to the calender for topping or frictioning.

The warming up system should be progressional, preferably allowing for working on two or three separate mills interconnected by strip conveyers before feeding the calender. By this means, any variability within batches of the compounded stock of rubber is largely eliminated and a uniform feed-stock temperature is achieved. While feeding, the maintaining of a regular bank in the rubber nip is important. Hand feeding billets of compound is undesirable, because at the time of loading, a temporary thickening of the sheet is almost inevitable. Strip feeding is extensively used taking advantage of a pendulum delivery for the top rubber nip.

The initial warming up of the calender rolls to operating temperatures takes several hours during which time they are well apart and rotated at low speed. It is also important to avoid stoppages of more than a few minutes during a calendering run to avoid excessive cooling. Irregular cooling of the roll surfaces can produce a periodic variation in the weight of rubber on to the fabric along with the length of the fabric which may be from 300 grams per sq meter to 500 grams per sq meter of the rubber.

The achievement of rubbering is also dependent upon the condition of the textile material. Unless a perfectly flat uniformly tensioned sheet is passed through the fabric nip, the calender operator must make frequent adjustments to the roll setting to prevent either fabric crushing or loose topping.

In the case of a three-roll calender, an alteration to the fabric nip does not affect the rubber layer thickness, since it is a movement of the bottom roll in relation to the fixed bearing middle roll. With a four-roll calender the stack or the breast roll type where the two top rolls are adjustable, the opening or closing of the fabric nip does, in practice, frequently result in a disturbance of the top roller nip.

It is interesting to know that experience has shown that difficult fabrics with respect to tension variability can be best handled on a three-roll calender.

Taking the example of a three-roll calender and assuming that the desired roll temperatures have been reached, the first operation should be to lower the adjustable top roll to a position known to approximate that of the sheet thickness required. Then with the calender still running at slow speed, a strip of fully warmed compound is placed in the rubber nip, and the layer is leveled by hand measuring the thickness of the sheet samples cut from each side of the sheet until a sheet of desired thickness is formed. At this stage the fabric nip is still open to permit the passage of the fabric which should have been drawn through the calendering machine at the end of the previous run to avoid dethreading and fabric waste on restarting. The calender is then stopped and the bottom roll is raised to a position judged to give an adequate pressure to impress the sheet of rubber into the fabric.

Having set the strip feed delivery in operation, the calender is restarted and maintained at slow speed and fabric is led. During this time the sheet is inspected for signs of crushing which are indicative of an excessively tightened nip or loose topping resulting from inadequate pressure. Should either of these faults be present, the appropriate action of lowering and raising the bottom roll is taken. Automatic trimming knives are also placed in position to cut the edges of the rubberized fabric sheet and the surplus rubber led away by rollers to be returned to the rubber nip or preferably to the warming mill. The speed of the calender may now be increased to maximum and any further correction to the rubber nip made as might be necessary. Thick or heavy sheet is prepared for chemical plant lining, molded goods, roll coverings and ebonite products.

The calendering process and its conditions are developed or modified according to the requirements of subsequent operations and the purpose for which the sheet is used. Thus for sheets which are to be open cured, such as in chemical plant lining and custom built items such as inflatables and ebonite pipes, roll coverings for paper and steel mills, the calendering needs to be more exact than the sheets which are used for blank preparation for molding of

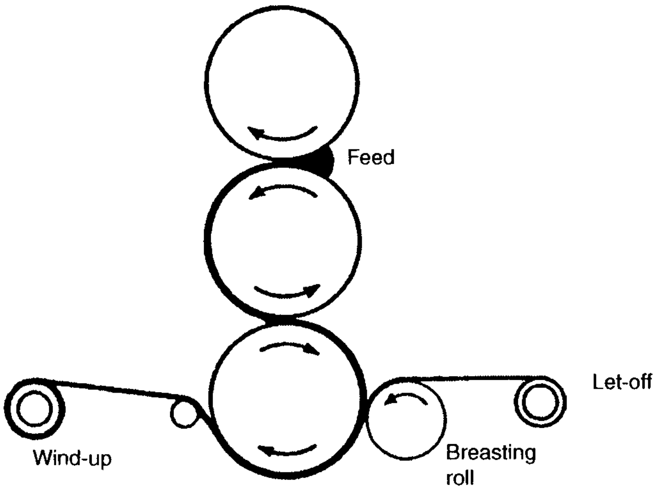

Figure 13.4 Plying up at the calender.

rubber components. Generally the higher the viscosity of the compound, the higher the calender temperatures have to be to give a smooth sheet free from v-shaped marks called "crows feet". On the other hand, the better the quality of the stock and the thicker the sheet and higher the temperatures, the more difficult it is to get a uniform sheet free from air bubbles or blisters. It will therefore be appreciated that each compound has to be calendered according to its own characteristics and purpose. Much depends on the skill and experience of the calender operator.

Calendering sheets for chemical plant construction and lining are usually required to be 4 to 5 mm thick. To obtain a satisfactory surface, the thickness is to be built up in plies of 1 mm or 0.8 mm thick sheets. The plying up at the calender is usually done by means of a rubber covered breast roll working against the bottom roll as shown in the above figure 13.4.

To get higher thickness of sheets up to 10 mm for equipment such as launders, ducts, agitators and thickeners, the plying is done in a doubling device which is custom built equipment.

14

Moulding Technology

Moulding of rubber products is a complex process with many variables which must be controlled. It is the operation of shaping and vulcanizing the shaped rubber which is in the plastic state by means of heat and pressure in an appropriate mould or form. Several moulded rubber components, constructions and structures are used in the process industry. The subject of moulding of rubber products has not been considered as an important one from the theoretical point of view for a long time. But the various complexities involved in the technology of rubber moulding or rubber forming certainly deserve to be pursued with quite a serious theoretical and fundamental study of the flow of rubber. The very important aspect in moulding or forming of rubber into different sizes and shapes of the product is the heat transfer to the stock of rubber, from the surface through the thickness of the rubber which ranges from 1/8th of an inch to anything as high as that for dock fenders, tyres, thick mountings etc. This effect is common to all processes involving heating by an external medium and can be solved by the well-known laws of heat conduction. Another point to be considered is the effect of thermal expansion of the rubber stock which is being raised to the vulcanization temperature. Since rubber expands much more than the metal of the mould, or the metallic form, it becomes obvious that if the mould is filled with the rubber blank and closed before the curing temperature is reached an enormous pressure is developed as the temperature rises. Such a high pressure produces an appreciable bulk compression so that when the mould is opened while it is hot there is a sudden expansion.

This expansion can easily cause the rubber to tear off at the flash line of separation of the two mould halves. This can be avoided by using a plunger type mould or by cooling the mould before opening or by loading the mould with a volume of stock that will just fill the cavity at the curing temperature. Low curing temperatures and suitable compounding to reduce expansion are also helpful.

14.1 Factors in Moulding

1) Time

In view of the high cost of mould and relatively large consumption of steam and electricity, economy means the shortest possible vulcanization time. Moulding time is directly proportional to the thickness of the product and inversely proportional to the temperature.

2) Temperature

As a rule-of-thumb, for every 10°C rise in temperature the cure time is reduced half. The heating medium in press curing of moulded products is either steam or electricity.

3) Flow period

Choosing the correct flow period is a very important aspect in the forming and shaping process. Mooney cure curves give good data on the flow period. The flow period also depends on the flow distances in the cavities of the mould and the viscosity of the rubber stock and the repeat pressure application cycles, called "bumping" cycles on the shop floor.

4) Control of scorch

Scorch time plays an important role in the reduction of moulding time as well as the thermal conductivity of the stock. Aluminium moulds are preferred, since aluminium is a better conductor of heat giving slightly shorter flow periods than steel moulds.

5) Moulding variables
The usual practical range of moulding variables during moulding of rubber are:

Moulding temperature (k) 293 to 500
Pressure in moulds (Mpa) 0.1 to 210
Shrinkage (%) 0.5 to 4.0

Moulds withstand the pressure necessary to cause flow in rubber and transmit heat to the rubber. They are usually made of cast steel or special alloys. The blank or the slug of rubber for a mould should be of such size that it will be slightly more than the full mould cavity or cavities. Simple mould may require only about 2% excess, while small but complex moulds may need up to 25% excess rubber.

14.2 Types of Moulding Process

Three types of moulding processes are available – compression, transfer and injection moulding. In compression moulding the rubber blank is placed directly into the cavity of the mould where it is heated by conduction which causes rubber flow by application of pressure. Transfer moulding uses prewarmed rubber which is heated during transfer and forced through small orifices into the mould cavities in a three-part mould. In the injection moulding process, the rubber compound is pushed under pressure from an injection head where it has been heated and plasticized into a closed heated mould where cure is completed.

Apart from the above three types there are custom built rubber products such as expansion joints, flexible cell covers and large size rubber foils for the caustic soda industry, and many inflatables, fabric reinforced products and thick moulded sheets for specialty applications in certain process plants. These are all hand formed in aluminium or cast iron moulds or forms by laying up process and then cured in autoclave. Here the flow of the un-vulcanized rubber during cure is not very important as the shape is already formed; rather the green strength and the stiffness of rubber stock with a low scorch time are the important requisites. A rubber expansion joint made by a hand layup method and cured in autoclave is shown in the following figure 14.1.

Figure 14.1 A hand fabricated rubber expansion joint for the fertilizer industry pipelines.

14.3 Press Curing

Certain products are custom built and involve special moulds which are either press cured or autoclave cured. These products may be either small hand-built belts, small size expansion joints, chemical resistant gaskets and anode carrying rings made from ebonite. The press provides the external source of pressure to form the products before vulcanization occurs. The essential features of a rubber hydraulic press are the head supported on columns or side plates and a cross head arranged to slide on the columns so that its upper surface is always parallel to the lower surface of the head. Pressure is usually applied from below to move the cross heads upwards towards the head. The pressure is applied by means of a hydraulic ram and cylinder working with a suitable hydraulic oil. An oil resistant sealing gasket fixed between the cylinder and ram prevents leakage of the hydraulic fluid. Hydraulic presses may have steam heated or electrically heated platens. The space between the platens where the mould is placed is called the daylight. To minimize heat losses, the platens are insulated by interposing a thick sheet of asbestos between the platens and head or cross head. Two or more daylights are often provided in a press to increase press productivity. The mould size is optimized to increase platen productivity. Sometimes platens may have slots and threaded holes so that moulds can be attached tightly to them. Thus, when the

Table 14.1 Comparison of compression, transfer and injection moulding processes

No	Compression moulding	Transfer moulding	Injection moulding
1.	Simple moulding	Complicated moulding	Intricate moulding
2.	Wrong sized blanks can cause flow lines, blisters and unfilled portions. Excessive size of blank is wasteful and causes heavy flash which is difficult to remove and causes dimensional deviatioins.	Excessive size of blank results in pot flash to the extent of 25%.	With automatic feeding stock size is controlled as well as quantity.
3.	Minimum flow occurs. The amount of flow is increased by applying bumping cycles (quick repeated application and release of pressure).	The compound must flow freely to fill the cavity properly.	The viscosity of the compound should be reduced to the lowest level to improve flow.
4.	Costly raw stock preparation and needs shaped performs.	Raw stock needs preparation such as pre warming.	Screw units masticate as well as heat the stock.
5.	Long cure cycles.	Moderate curing cycles.	Very fast curing cycles.
6.	High labour cost since each cavity of the mould should be loaded individually.	Moulds are heavy and operator involvement is high in loading and unloading.	Operator only unloads the moulded articles.
7.	Suitable for low productivity.	Suitable for medium scale production.	Large volume production is possible.
8.	Low cost of production.	High cost of production.	Cost depends on production volume.

Table 14.1 (cont.) Comparison of compression, transfer and injection moulding processes

No	Compression moulding	Transfer moulding	Injection moulding
9.	Mould wear is less.	Mould wear is high.	Mould wear is high.
10.	Inexpensive sheet metal, bars or rods are used for mould construction.	Mould cost is high.	Mould cost and its material cost is high.
11.	Expensive finishing operation is involved because of flash.	Pot flash is up to 25% and as such costly finishing operation is involved.	Negligible flash occurs, and so finishing cost is low.
12.	Heat transfer is from metal to rubber compound.	Compound gets heated up as it flows from the pot to mould cavity.	Screw and injection heat the compound to curing temperature.
13.	Moulding temperature range is 120°C to 160°C.	Moulding temperature range is 130°C to 170°C.	Moulding temperature range is 180°C to 240°C.
14.	This method is often used for heavy mouldings. Inserts in a mould cavity tend to be displaced as they are positioned in an open mould.	Often used for metal inserts. Better adhesion of rubber to metal or fabric is obtained.	Specialty elastomeric compositions are to be designed to make high quality products.

press opens it also opens the mould. A table can be fixed in front of the press platens to push the moulds in and out into the daylight. For multi-daylight presses, the tables are adjustable for required height by hydraulically operated cylinders.

14.4 Moulding of Hollow Parts

Hollow rubber parts may have a small opening such as in hot water bottles or in many chemical and medical industry applications, or may be completely closed as in play balls, or with round metallic cores encompassed within balls which are used in scrubbing operations in some separation processes in the chemical industry. After the curing is completed, the neck of the hollow part is stretched considerably in order to remove the part from the core. A jet of air may be blown between the neck and the core so as to stretch the neck. In the case of hot water bottles the screwed stopper is separately moulded and fixed to the neck of the bottle by the combined use of an adhesive cement and a thin metal band applied tightly to the outside of the neck. Products which are inflated within the mould during curing such as play balls are made of a preform which encloses a quantity of blowing agent. The preform is placed in a simple two piece mould which is then closed. As the blowing agent decomposes in the heat of moulding, gas is produced and the pressure of the gas forces the rubber against the hot mould surface to complete the cure. Balls for critical uses such as for scrubbers in process equipment must be more accurately made since they should meet specifications of size and weight along with bouncing characteristics and chemical resistance.

14.5 Moulding Shrinkage

All rubber products exhibit shrinkage after cure, mainly due to the thermal expansion which occurs at vulcanization temperature. Moulded rubber goods are never as big as the moulds in which they are cured. The difference between the dimensions at room temperature of the finished goods and of the mould expressed as a percentage is called the shrinkage from mould dimensions.

$$\text{percentage moulding shrinkage} = \frac{\text{dimensions of the mould} - \text{dimensions of the article}}{\text{dimensions of the article}} \times 100$$

The amount of shrinkage depends mainly on the difference between the thermal expansion coefficient of vulcanizate and mould material at the vulcanization temperature. Shrinkage is affected by factors such as curing temperature, and the level of filler loading in a rubber compound. Higher filler loadings reduce shrinkage. On cooling to room temperature the rubber article contracts more than the mould, because it has a considerably higher thermal coefficient. As a rule-of-thumb, mould shrinkage is about 2% for NR compounds. For synthetic rubber compounds it is slightly more, which also depends on factors such as compounding ingredients and their dosage levels and cure temperature. The dimensions of the moulded goods often have to satisfy very strict requirements in many engineering applications. Therefore, it is important to know their shrinkage so that the mould can be designed after comparing reference dimensions of the cooled moulded article with those of the cold mould cavity which produced it.

Shrinkage of rubber is sometimes desirable, because if the rubber and the mould had the same coefficient of expansion, it would be much more difficult to remove the vulcanizate from the mould. In multi-cavity moulds the individual cavities may sometimes vary in dimensions and shrinkage, and therefore each cavity must be measured separately for acceptability of dimensions in the mouldings produced. Difference in moulding temperature may lead to a different degree of shrinkage. Shrinkage can be reduced by curing at low temperatures. As a general rule the larger the rubber content, the higher the expansion coefficient of rubber. The larger the filler loading, the lower the shrinkage because the thermal coefficients of the fillers are lower than those of rubber. In transfer and injection moulding processes the shrinkage is often less.

14.6 Mould Lubricants

Materials which prevent sticking of the rubber to the mould surface facilitate the removal of the articles from the mould and prevent the formation of crust. These materials are called mould lubricants. They are applied to the mould and not to the rubber. Silicone emulsions are the most widely used lubricants as they offer effective release properties and give a smooth glossy surface finish. They are most effective also because they have a higher thermal conductivity facilitating longer use. The silicone withstands temperature up to 200°C. Neutral soaps are also popular as mould lubricants. These lubricants are applied by means of brushes or by spraying. The application of these agents should be minimum as otherwise they interfere in mould flow resulting in faulty mouldings due to poor knitting of the compound. The presence of silicone and similar materials can be extremely detrimental to rubber-to-metal bondings and cause debonding of the rubber-to-metal parts. Extremely well finished (i.e., chromium plated and polished) moulds facilitate easier removal of moulded parts.

14.7 Moulding Defects

Moulding defects up to 5% are allowed in the moulding operation. The common moulding defects and their causes and remedies are given in the following table 14.2.

Table 14.2 Moulding defects

Defect	Cause	Remedy
Backrinding	Rupture at parting line.	Cure at low temperature and high pressure.
Blisters	Air trapped in blanks.	Modify the processing to a low temperature level and prick out the blisters while in unvulcanized state.
Flow cracks.	Incorrect shape and size of blank, incomplete mould flow high viscosity stock and excessive mould lubricant.	Modify the shape, reduce temperature, modify curing system, peptize and pre warm the stock.
Porosity-generally inside the centre	Under cure and reduced pressure.	Increase time, temperature and pressure.
Tearing	Bad mould design, low hot tear strength of compound, overcure and careless removal of moulded article.	Avoid sharp edges, improve compounding technique, cure at optimum level and use simple devices for removal.
Sticking to mould.	Dirty mould, inadequate lubricant and undercure.	Frequent cleaning and proper maintenance of moulds and proper application of mould lubricant.

Table 14.2 (cont.) Moulding defects

Defect	**Cause**	**Remedy**
Excess flash	Excessive stock loading, improper mould aligning, low pressure and improper mould design.	Loading blanks of correct weight, increase moulding pressure and replace loose dowel pins in the mould.
Rough surface distortion	Use of scorched blank, less mould flow time, slow closing of the mould.	Reject seemingly scorched stock, correct ram speed.
Blooming	Undercure, low moulding pressure, low temperature.	Correct heating device, ram movement and improve compounding.

15

Service Life of Rubber-Lined Chemical Equipment

The ageing of rubber has been a nuisance as evidenced by many examples in the early history of rubber, since the time of MacIntosh, Hancock and Charles Goodyear [1]. Much noteworthy scientific work was done on the causes of the deterioration of rubber, mainly due to the oxidation effects.The earliest sign of decay due to ageing of a vulcanized rubber is a loss of tensile strength. Upon continued ageing process in service there is an increase in weight ranging from 2% to 10%. From the point of view of a chemical reaction, it is obvious that rubber gets oxidized in air since 85% of it is unsaturated. It can be surprisingly noted that rubber is still stable withstanding this kind of deteriorating chemical reaction.

Apart from oxygen, there are other deteriorating influences which accelerate the ageing process. In heavily loaded rubber vulcanizates, due to the action of light, air and rain, chalking of rubber and fungus formation occur. The surface layer deteriorates and exposes the fillers. Another condition occurs namely sun-checking of stretched rubber in sunlight. Unstretched or highly stretched rubber cracks less than rubber stretched to the critical elongation, which is approximately the same as that for maximum ozone cracking. Ozone has little effect on unstretched vulcanized rubber. The cracking effect of a stretched vulcanized rubber is more serious at 5% to 10% elongation than at either higher or lower elongation. The critical elongation for maximum cracking varies with the types of vulcanizate.

When rubber is used at high temperatures, even in the absence of oxygen, a change known as heat deterioration occurs due to internal heat generated during service, leading to blow-out or bursting. Operations at elevated temperatures reduce the ultimate elongation of the rubber. Continued vulcanization is not always harmful for the stiffening caused in this manner. It can offset the softening due to the action of heat and swelling in certain cases [2,3].

In spite of the unsaturation of rubber it is said to be resistant to chemical attack since a few chemical derivatives like chlorinated rubbers, cyclised rubbers and chlorides are formed as protective layers retarding further attack by the chemicals. Properly compounded vulcanizates satisfactorily resist the action of most inorganic acids other than oxidizing acids such as nitric, hydrochloric and sulphuric acids. Rubber linings which are to resist swelling to a lower degree should be "tightly" vulcanized.

The effect of heat ageing on ebonite has been a subject of interest for quite some time. It was noticed that softening occurs in heat ageing of ebonite followed by lower hardness and impact strength. It is quite interesting to know the investigation on semi-ebonite made by Gribbons reported in the Transaction of the Institution of Rubber Industry 11, No.3 (1935) [4], as it has a practical significance. It was known that as rubber is progressively vulcanized with sulphur, it passes from the soft vulcanized stage through a short, brittle, over-vulcanized condition to a state where it resembles leather in pliability and finally becomes a hard rubber or ebonite. There was a general belief that all products between normal soft vulcanized rubber and ebonite are susceptible to rapid oxidation and subsequent decay. It was demonstrated by Gribbons that a leather-like material was obtained with compounds containing between 22% and 25% of sulphur on the rubber, vulcanized for 4 to 5 hours at about 148°C. Such a product contains almost exactly one-half the proportion of sulphur required to produce fully saturated ebonite. The rate of oxidation of these semi-ebonites in air at 70°C was shown to be astonishingly slow. The action was essentially of a surface character and even after 8000 hrs at 70°C, the increase in weight was little more than 10 grms per square meter of surface. An oxidized film was formed on the surface and this film showed folds on bending the semi-ebonite with further heat ageing, the surface became hard and smooth and cracked rather than wrinkled when flexed. Experiments indicted clearly that oxidized film formed on the surface during early ageing protected the interior for a longer period. The research showed that between the two stable rubber sulphides corresponding to the soft-vulcanized state and to ebonite, there is a third stable sulphur compound with very valuable characteristics containing about half the sulphur necessary to saturate all the double bonds in the unsaturated rubber.

When fully cured ebonite is exposed for a considerable period to the action of sunlight in the presence of humid air, the black surface changes its colour and assumes a green or brown tint. These changes are superficial since the colour can be restored by buffing of the surface layer.

15.1 Materials that Improve the Ageing of Vulcanizates

The commercial significance of the ingredients used in rubber compounding to improve resistance to ageing accelerated work on the discovery, development, use and manufacture of new products. The development efforts were competitive in nature, each manufacturer claiming superiority of their products over the others. Some of the age retardants are listed below.

15.1.1 Accelerators

Many accelerators greatly improve the resistance to ageing of the rubber vulcanizates. In general, dithiocarbamates, aldehydeamines and mecaptobenzothiozole derivates improve the ageing properties of rubber especially when used in comparatively large proportions together with low proportions of sulphur. This method of retarding deterioration of rubber is being utilized more frequently in rubber compounding.

15.1.2 Phenols

Phenols have definite protective action. Examples are P-hydroxybiphenyl, hydroquinine and pyrogallol, methylene di-b-napthol.

15.1.3 Primary Aromatic Amines

These were first investigated and used in rubber as accelerators. Their effect in improving the vulcanizing and ageing properties of rubber was utilized for several years. Primary diamines, primary secondary amines and aminophenols are much more active than simple primary amines. Aminophenol and phenolamine salts are effective antidegradents.

Diphenyl guandine, especially, is an effective antidegradent for ebonite compounds. The technique of rubber compounding is now in an era of rapid advance. Great inroads have already been made in this area with special emphasis on resistance to ageing of rubber and improvement of its service life. Practical methods of protecting rubber against oxidative deterioration and against corrosive chemicals have increased its life manyfold and have put the theoretical investigations of the causes of the various effects into doubt. Especially in the case of protective lining compounds, where only the inertness of fillers are considered most rather than their reinforcing abilities, the compound formulations are looking very dissimilar with other known compounds for general engineering applications. The excellent search for means of retarding the deterioration of rubber has provided a mass of information which led finally to a full understanding of its structure, properties, and mechanism of reaction with various corrosive environments. At this juncture development in the area of newer filler types for admixing with rubber looks to be an interesting area for research for developing compounds for more severe duty conditions which the chemical process industries might be facing in the future.

It is worthwhile to consider other conditions which cause degradation of rubber. Because of their chemical nature rubbers are subjected to chemical degradation and mechanical damage during storage and service. For many applications ageing effects may not be serious, since catastrophic failure never occurs due to the normal ageing process. Failures often occur due to the malfunction of the product because of its improper design and selection of materials to manufacture the same. However, the consideration of ageing is much more serious in the case of anticorrosive lining applications where the combined effects of oxidation, progressive chemical degradation, diffusion and swelling due to fluids occur. Rubber lining failure and prediction of its service life is a complex matter to be dealt with. The fundamental reaction responsible for the ageing of both natural and synthetic rubbers is the oxidation of the rubber hydrocarbon by oxygen. The oxidative degradation is activated by heat and stresses due to flexing.

Peroxide radicals are formed as a result of initiation of the reaction of oxygen with the hydrocarbon, which further reacts with the rubber hydrocarbon forming cyclysed radical which then adds to the oxygen molecule again and the chain reaction continues until the rubber is degraded. The nature of change that is observed as a result of oxidation depends on the type of rubber and the ageing condition to which it is subjected. The net effect on the physical properties of the rubber is the result of two reactions, namely chain scission and cross linking. Natural rubbers and butyl rubbers are more susceptible to chain scission reaction leading to reduction in tensile strength. The butadiene rubbers as well as neoprenes are characterized by a greater susceptibility to cross linking reaction resulting in a loss of elasticity, which can be measured by a decrease in elongation and increase in modulus. If the modulus changes during the life of a product, it means that the rubber has lost its elasticity and has become brittle, indicating complete absence of elasticity in the rubber. Factors affecting ageing of rubber are described below with more details.

15.2 Oxidation

Addition of even 1% to 2% combined oxygen is sufficient to cause significant deterioration of properties for most rubbers [5]. Oxidation proceeds by free- radical mechanisms and leads to chain scission and cross linking. In chain scission, free radicals attack the polymer backbone causing softening and weakening. This is the primary effect noticed for natural rubber and butyl rubber oxidation. Brittle stocks result from attack at cross links, resulting in formation of new cross links. This is predominant with SBR, neoprene, nitrile and EPDM. Loss of elongation is the most sensitive criterion for ageing measurement and it is favoured over measurement of tensile loss for cured compounds.

15.3 Heat

Heat accelerates oxidation. Because oxidation is a chemical reaction, an increase of 10°C in temperature almost doubles the rate of oxidation. This means that the rate of oxidation is at least 2^8 times faster at 100°C than at 20°C. Accelerated ageing tests conducted in the laboratory at ambient temperatures as well as elevated temperatures provide useful data regarding the behaviour of rubber.

Falloff in tensile strength, modulus and elongation as the temperature rises is due to accelerated degradation of the rubber. Irrespective of the type of base rubber used, the physical properties of rubber fall as the temperature is increased to above 120°C due to molecular breakdown. Since rubbers lose their physical properties at higher temperature they become weak and as such susceptible to chemical attack.

15.4 Flexing

Flex cracking involves not only a mechanical fatigue but also an oxidation effect that is accelerated by the heat generated during flexing. The higher the rate of flexing the higher the heat generation and the worse is the fatigue life. Mechanical flexing leads, therefore, to serious reduction in the useful life of the rubber products.

15.5 Ozone

The ozone concentration in the atmosphere is only a few pphm. In certain chemical plants as in electrolytic mercury cell houses in the chloralkali industry, the ozone concentration is higher. Although the atmospheric ozone level is low, it reacts with rubber double bonds rapidly and causes cracking of rubber products. Especially when rubber is under stress (stretching and bending as in the case of flexible cell covers), the crack development is faster. Neoprene products resist thousands of parts per hundred million of ozone for hours without surface cracking. This nature of neoprene is quite suitable for cell house application in chlor-alkali industries. Natural rubber will crack within minutes when subjected to ozone concentration of only 50 pphm.

15.6 Light

Ultraviolet light promotes free-radical oxidation at the rubber surface which produces discolouration and a brittle film of oxidized rubber. This skin cracks in random directions to form a pattern called crazing, which can be prevented by the addition of carbon black fillers or UV stabilizers. Black stocks are more resistant to UV light than are gum or light coloured stocks. Non-black compounds require larger quantities of non-staining antioxidants which should bloom to the surface as the surface-UV stabilizers deplete.

15.7 Sulphur

Low sulphur stocks have better ageing resistance. Normally the oxidation rate increases with the amount of sulphur used in the cure. The increased rate may be due to the activation of adjacent C-H groups by high levels of combined sulphur. Saturated sulphides are inert to oxidation.

15.8 Metals

Metal ions such as iron, copper, manganese and cobalt, when present even in small amounts, accelerate rubber oxidative reaction by affecting the breakdown of peroxides in such a way as to accelerate further attack by oxygen. Therefore these metals and their salts such as olieates and stearates which are soluble in rubber should be avoided. In general, the standard antioxidants do not give protection against metal ions. Because the activity of the metal depends on its being in an ionic form, it is possible to protect stocks by incorporating substances which react with ionic metals to give stable complexes.

In cell houses, cracks can be visually seen on the upper neoprene surface of the flexible covers which are subjected to stress at a temperature of 80°C, during eighteen to twenty four months of operation, necessitating mandatory replacement of the covers. Ozone reacts with double bonds so rapidly that it has no chance to diffuse into the rubber and therefore all action is at the surface. Thus it implies surface protective agents are most useful against ozone attack. For example, waxes that bloom to the surface of rubber to form an inert film are used effectively for static protection.

Antiozonents protect the rubber surface by the formation of a protection layer, the ozonides on the surface of rubber by reaction of the antiozonents with ozone. Certain polymers also provide good ozone protection. The use of 10-20 parts of EPDM, a low diene rubber, in natural rubber compound significantly increases ozone resistance.

15.9 Fluids

According to Faraday [6] when rubber is immersed in fluids, the surface layer of rubber immediately swells and during the initial stages, the lateral expansion is prevented by the underlying un-swollen material. Thus a two-dimensional compressive stress is produced in the surface leading to surface instability, corrugations etc. With swelling, the rubber is strained and its physical properties change. If there is no chemical change taking place, the swelling phenomenon can be considered as a reversible one and physical in nature. However in many of the actual operating conditions, the reversible process of swelling and deswelling rarely occurs. Due to swelling, the rubbers retain only below-optimum physical properties. The volume change due to swelling produces changes in the tensile strength.

The testing procedure of properties of elastomeric vulcanizates after immersion in organic liquids is common for both natural and synthetic rubbers. ASTM D171-66 [7] used for this purpose serves as a method for estimating the comparative ability of rubbers to withstand the effects of liquids by examination of the material after removal from the liquid. However proper testing of the physical properties on swollen rubber poses many problems.

Zanker of Kiriat-Tam G, Israel in his paper on "How to determine tensile strength of vulcanizates after immersion in liquids" [8] examined the changes in weight, in volume, in elongation, in hardness and in tensile strength of rubber after immersion. The procedure for tensile strength determination was based on two consecutive measurements of an original specimen and of a specimen after immersion. These data are then used in the calculation of the tensile strength of the specimen based on the swollen area. A detailed description is found in ASTM D171-66 itself. The calculation performed is according to the following formulae:

$$T_1 = T_2 / (1+V/100)^{2/3} \qquad (1)$$

where T_1 = tensile strength of the specimen (in approximate units) on the swollen area.

T_2 = tensile strength of the swollen rubber specimen (in approximate units) based on original, unswollen cross-sectional area.

V = percentage change in volume. The percentage change in volume may be calculated as below:

$$V = (W_3 - W_4) - (W_1 - W_2) / (W_1 - W_2) \times 100 \quad (2)$$

W_1 – initial weight at specimen in air, g
W_2 – initial weight of specimen in water, g
W_3 – Weight of specimen in air after immersion – g
W_4 – Weight of specimen in water after immersion, g

In special cases, when the geometrical shape of a specimen is simple, its change in volume can be estimated by means of a simple measurement of its dimensions and multiplying these according to geometrical formulas for volume determination.

The experimental procedures as described above and the results thereon give satisfactory data on the behaviour of rubbers immersed in fluids of various kinds and can be correlated with practical observation.

The expectancy of rubber lining life is very difficult to predict. The service life of the rubber lining is dependent on several factors under the control of the manufacturers and the applications of lining. The various determining factors of rubber linings are:

1. Frequency of filling and draining of the acids in the tank / vessel.
2. The difference in temperature between the acid solution and the outside temperature. A low and steady temperature results in a longer life such as in storage tanks.
3. Colour of paint, chosen for exterior of rubber lined tanks can make a difference. A light colour will lower the temperature inside of the tank and a dark colour will radiate the heat especially in storage tanks.
4. Rubber linings will dry out and get oxidized in atmospheric oxygen. Therefore it is better they remain submerged longer in fluid media so that they will last longer.

15.10 Predicting Life of Lining

Scientists form CSIRO, Australia and Monash, University [9] have developed a technique that can evaluate the condition of rubber products such as conveyor belts. The technique uses Nuclear Magnetic Resonance (NMR) which involves subjecting the sample into a magnetic field to measure the condition of rubber. This technique can result in the development of a hand-held scanning device to check rubber products while they are in service eliminating the need to take samples. This means that we can get the full life out of the rubber products but replace them well before they fail. However CSRIO's Dr. Anita Hill says that unfortunately rubber performance degrades over a time due to ageing. Rubber ageing results in a loss of flexibility, abrasion resistance and elasticity. For many abrasive and erosive application such as in mining or in the ore industry and transporting system handling abrasive liquids and solids, oxidative degradation is not a concern, because the rubber lining would have been worn out before any significant oxidative ageing effects occur. However, sudden and unexpected rubber degradation can lead to catastrophic failure in chemical process industries. The degradation of rubber is very difficult to predict, because the rate of degradation depends on many factors such as temperature, chemical corrosive environments, loading condition and the type of rubber chosen. Current inspection techniques for checking the condition of rubber rely on observing the effects of ageing in service, for example cracks or tears in rubber, blisters and debonding - by the time these appear it can be too late to prevent failure. The new technique, the scientist claims, will give earlier warning if a rubber part is degrading or losing elasticity, so that it can be replaced well before failure occurs. The scientist's research has been applied to the failure analysis of rubber conveyor belts and process tank linings. NMR technique can be used to characterize the polymers in the rubber so that over a time period, we can detect molecular symptoms of rubber ageing, such as changes in polymer chain length, cross linking and the presence of degradation products.

15.11 Hydrochloric Acid Tank Lining Life

Hydrochloric acid once named as muriatic acid is a strong highly corrosive acid. The commercial concentrated or fuming acid contains 38% hydrogen chloride. For storage tanks and tankers natural rubber lining on steel has predominantly been used for this acid service. The acid reacts with natural rubber hydrocarbon to chlorinate the surface making an impermeable membrane. In concentrated hydrochloric acid, it takes approximately three to four months for natural rubber crust formation which is in the range of 1/64" depth.

This crusting effect makes natural rubber an excellent lining for HCl service. It is also the destructive mechanism of the lining in the later years. As surface stress cracks develop the acid penetrates the rubber forming a new surface crust. This cycle continues until complete lining failure eventually occurs. Lining performance life has been reported by many chemical factories to be in the range of 7 to 20+ years depending on hardness of rubber, temperature conditions and stresses on the vessels. Through the years, the history in some caustic soda industries has demonstrated that a pure gum natural rubber gives the longest lining life for concentrated HCl acid. In general, the lower the shore hardness, the longer its life in the concentrated acid. For example a 50°A/55°A durometer natural rubber will reach 75°A/80°A after three months, where as a 40°A/45°A durometer natural rubber takes a longer time to reach 75°A/80°A.

Contrary to this a 60°A durometer natural rubber is better for dilute 10% to 20% HCl. In dilute acid service, the compounded natural rubber has better water absorption than soft gum rubber. Inspection on the rubber lined tanks shows that HCl vapours are more detrimental than HCl liquid to lining ageing. To improve the natural rubber life in the vapour phase, a chlorobutyl thin lining or coating can be given on top of the NR lining since chlorobutyl has a greater tolerance to HCl vapours and is less affected by heat ageing. The hardness change with chlorobutyl is not appreciable when compared to natural rubber.

15.12 Residual Life of Natural Rubber Lining in a Phosphoric Acid Storage Tank

A huge phosphoric acid storage tank of size 24 m dia x 14.4 m high, in the harbour terminal, one of the largest storage tanks in the world in a fertilizer plant which has been rubber lined with a phosphoric acid resistant natural rubber lining of thickness 5 mm of durometer hardness 55°A in India, was observed after 10 years of service life. The rubber lining was done with a prevulcanized calendered sheet using self-curing bonding adhesive based on neoprene. During inspection of the tank after draining out the acid, the rubber lining was found to be intact in appearance, free of any blisters or visual damage. However to find out the residual life of the lining, tensile strength measurements were taken on a cut portion of the lining which was later patched up with a piece of fresh sheet. The tensile strength as measured was 42 kg/cm^2 tested in a conventional manner. The tensile strength of the original fresh lining sheet measured after 7 days of cure was 129 kg/cm^2. There is a substantial fall in the tensile strength after a life of 10 years. Hardness value does not show much variation due to swelling of the sheet, even though it might have been hardened due to oxidation by dissolved oxygen in the medium. Using the Lagrange's interpolation formula:

$$Y = (x-x_2) / (x_1-x_2) \text{ X } Y_1 + (x-x_1) / (x_2-x_1) \text{ X } Ys_2$$

where Y = total life of the lining

Y_1 = 7 days (after curing the fresh sheet)
Y_2 = 10 years (life period)
$x = 1$
$x_2 = 42$
$x_1 = 129$

The total life was calculated under normal ageing condition. When the rubber is totally degraded, the value of tensile strength tends to a limiting value of 1 kg/cm^2 which is an assumed figure (x).

The total life as per this interpolation formula was found to be about 15 years and the remaining life was predicted as 5 years.

Though the formula was indicative based only on the fall in tensile strength of the rubber, other factors like bonding, strength, visual appearance were not taken into consideration. A total sudden failure cannot however be anticipated in this case, since a 10-year life was considered as good enough for protecting the mild steel tank with the rubber lining. Using the tank beyond 10 years is somewhat risky in spite of the fact that the rubber lining appears to be intact superficially.

15.13 Immersion in Fluids

The ageing of polymers immersed in fluids is of considerable importance in several lining applications. The acid resistance is a complex multidimensional property that cannot be defined solely by relative volume or weight change values after immersion. The strength and elastomeric properties are drastically affected by acid / fluid exposure and the correlation of the degree of degradation and volume / weight changes are not linear. As swelling occurs the rubber is strained and tensile strength, modulus and hardness decrease whereas resilience increases. The swelling media can provide some protection against oxidative degradation due to the exclusion of the oxygen. Studies have shown that a neoprene compound shows cracks if bent and kept in air at 150°C for 80 to 100 hrs. If it is kept at the same temperature in bent position but immersed in a heavy engine oil it lasted for 600–800 hrs. In addition to the longer life at a given temperature, immersion in fluids often means that a rubber resistant to the immersion fluid can be used at a higher temperature than when exposed to hot air.

It should be noted that different properties are affected to different extents by swelling. Current methods of measuring physical properties of rubber are not entirely satisfactory if used for swollen rubbers. In the case of chemical plant linings, there are many associated problems, such as bonding strength of the lining with the metal, corrosion product formation resulting in reduction in thickness of lining and increase in thickness of lining due to swelling. The tensile strength of the lining is of low significance, from the chemical resistance point of view. The tear strength is very important because of its variation due to mechanical strains of acid slurries leading to physical damage of the lining. Although the strength properties of rubber are affected by the degree of swelling, a useful indication of the performance and ageing of rubbers for chemical plant lining can often be obtained from swelling data rather than the data of variations in physical properties. A reasonable conclusion of lining life is possible when immersion tests at simulated condition are conducted and the swelling data like increase or decrease in thickness measured.

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16

Case Studies

Selection of suitable materials of construction is an important step in the design of plant and equipment for the process industry. Case histories of engineering failures and disasters as well as success stories on account of material selection are eye openers for understanding design faults or design perfections as the case may be. Materials can fail due to different failure mechanisms such as elastic deformation, plastic deformation, fracture, crack, fatigue, creep, environmental, thermal and chemical attack and wear or erosion or abrasion caused by dry or wet solids, gases, fumes and atmospheric oxygen and ozone. The failure process as well as successful equipment performance depend on the properties of material or its composites and the way in which it is used in the final component or structure. Most failures can be avoided through a study of case histories. We learn from actual failures and success stories described in case histories. We come to know what went wrong in a material selection through case studies. Mostly all designs are based on trial and error and at times intuitive sense and not backed by any proper calculations and numbers. Very comfortable factors of safety are applied many times during the design and fabrication of a structure, component or equipment. Since designs can be established by mathematical calculations and methods, it is generally assumed that engineering failures cannot occur. This cannot be taken as true always because of the fact that practical and state-of-the art technology can supersede theoretical consideration very often. It is clearly to be understood that learning from case histories of past mistakes and successes is an essential part of safe and proper selection of materials to efficiently design the plant and equipment. Case histories and case studies also teach one to select alternative materials of construction on economic and performance consideration. Several case histories can be cited on the topic covered in this book. A few of them are discussed below.

16.1 Case Study

Space Shuttle Challenger Disaster

The disaster to the space shuttle Challenger is a case study of untimely use of a rubber O-ring by the mechanical engineers. The supplier engineers knew that the rubber seal has very limited sealing capability at low temperature use, but they could not prove this in a space shuttle launch situation. In spite of the reservations of the supplier engineers, the shuttle engineers went ahead in launching the space shuttle on a freezing cold day. The space shuttle disaster occurred on January 28, 1986, when Space Shuttle Challenger broke apart 73 seconds into its flight, leading to the deaths of its seven crew members. The spacecraft disintegrated over the Atlantic Ocean, off the coast of central Florida, United States, at 11:39 a.m. EST.

Disintegration of the entire vehicle began after an O-ring seal in its right solid rocket booster (SRB) failed at lift-off. The O-ring failure caused a breach in the SRB joint it sealed, allowing pressurized hot gas from within the solid rocket motor to reach the outside and impinge upon the adjacent SRB attachment hardware and external fuel tank. This led to the separation of the right-hand SRB's attachment and the structural failure of the external tank.

The crew compartment and many other vehicle fragments were eventually recovered from the ocean floor after a lengthy search and recovery operation. Although the exact timing of the death of the crew is unknown, several crew members are known to have survived the initial breakup of the spacecraft. However, the shuttle had no escape system and the astronauts did not survive the impact of the crew compartment with the ocean surface.

The disaster resulted in the formation of the Rogers Commission, a special commission appointed by United States President Ronald

Reagan to investigate the accident. The Rogers Commission found that NASA's organizational culture and decision-making processes had been a key contributing factor to the accident. NASA managers had known that contractor Morton Thiokol's design of the SRBs contained a potentially catastrophic flaw in the O-rings since 1977, but they failed to address it properly. They also disregarded warnings from engineers about the dangers of launching posed by the freezing cold temperatures of that morning and had failed to adequately report these technical concerns to their superiors [1,4].

See fig below [2].

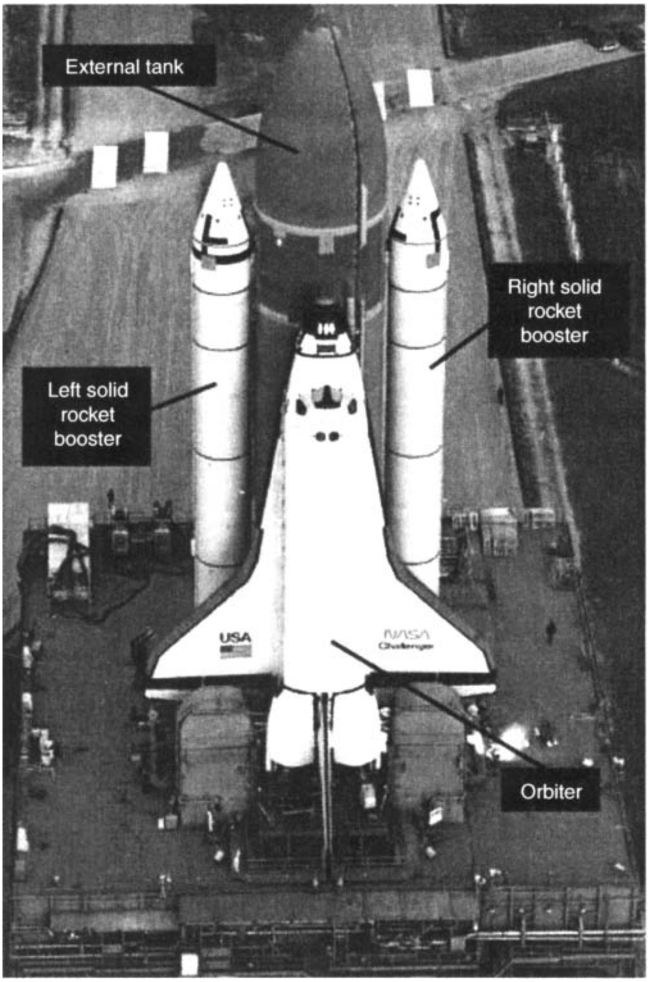

Figure 16.1 Picture of Challenger. http://www.orgs-evolution-knowledge.net

16.2 Case Study

Hinkle Reservoir

The Hinkle Reservoir in Granite Bay, CA, (see picture below) has been a pioneer in floating reservoir covers, since its reconstruction in 1980. It has attracted many engineers, administrators and legislators from the US and abroad, to learn about successful design for floating reservoir covers manufactured from Hypalon rubber [3]. And now, after decades of life Hinkle Reservoir is still going well and attracting onlookers, due to its durable engineering design with DuPont's Hypalon synthetic rubber as cover membrane, According to Jim English, General Manager, based on recent forensic tests performed, the reservoir with its floating cover, "has been an amazing success, and a practical and economical solution" for the San Juan Water District (SJWD). When the reservoir was initially reconstructed, alternatives such as steel and concrete tanks with rigid covers were considered. And the cost of concrete tanks and rigid covers was "too high." The cost-effective solution came in the form of proprietary patented design principles of a floating cover based on Hypalon from Burke Industries, in San Jose, CA USA. The cost of the floating cover design was in the range of 60–80% less than the other alternatives considered. The Hinkle Reservoir provides quality water resources to more than 265,000 people annually in the Sacramento, CA region in the US. It has an approximately 62 million gallon capacity, with a 12.5 acre surface area. The floating cover, when fully extended, is almost 14 acres in size. During the summer, the reservoir turns over two times per day. The winter months are much slower, with turnover being every 2–3 days. With the large amount of people that the reservoir serves, as well as the rate of water turnover, performance of the floating cover membrane is critical. With the initial 25-year warranty on the floating cover nearing its close, and to assess how well the cover was still performing, the authorities recently contracted an independent outside firm to test the membrane. The independent contractor who was hired did destructive testing and all the appropriate forensic tests on a number of samples cut out of the Hypalon based floating cover membrane. The results came back impressive, according to Mike O'Bleness, Water Quality Manager. The tests showed that potentially another 20 years of service out of the cover was possible. Additionally, it holds chlorine residuals very well. The loss of chlorine was 1/10th

Figure 16.2 Picture of The Hinkle Reservoir in Granite Bay, CA Courtesy Dupont, USA.

of a part of chlorine, which was considered to be *excellent*. Prior to the installation of the cover, the Hinkle Reservoir had been losing hundreds of tons of chlorine to evaporation. The water quality has remained essentially constant over more than two decades. The cover has been relatively easy to maintain, and has successfully stood up for decades of time. And finally, recent forensic tests have shown that the cover potentially still has a long service ahead.

16.3 Case Study

Ammonium Nitrate Explosion

An accident [5] occurred with a closed hollow shaft of a screw conveyor with dimensions, length 7 m, diameter 250 mm, and wall thickness 6 mm, which was used for transporting the raw materials and the recycle in the granulating plant in an ammonium nitrate plant. The shaft of this screw conveyor had a weak spot with a hole at one place, caused by scouring. The shaft was repaired by welding around the weak spot with the hole. While carrying out this welding job on the hollow shaft, two men were working on the third floor of the building, lining the hopper of the screw conveyor with rubber sheets. At that moment the shaft burst with explosive force, and one man standing on top of the screw conveyor and engaged in rubber lining was killed instantaneously. The other man was thrown over the guard rail and landed on a floor 18 m. below. This man died in the hospital.

After investigation it was found out that the hollow shaft was contaminated with NPK-type fertilizer through the hole at the worn spot. The nitrate-containing fertilizer had been ignited by the heat from the welding. A self-sustained decomposition started after closing the hole and the shaft burst.

The above serious accident shows that welding of mild steel equipment where the rubber lining is being done could be very dangerous, and it should be noted as a rule that during rubber lining no welding activity should be carried out in the nearby areas and no welding should be done on a rubber lined equipment. Even while welding is necessarily to be done in other areas which are not required to be rubber lined, precautions should be taken beforehand.

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Dt:11/6/67

16.4 Case Study

"O" Ring Failure

During a routine transfer of liquid hydrogen from a commercial tank trailer to a receiving vessel, a leak developed in the bayonet fitting at the trailer/facility connection. The leak produced a fan-shaped hydrogen vapor spray which enveloped the rear of the truck where the hand-operated shutoff valve was located. Emergency-trained personnel, wearing protective clothing, entered the area of the dense spray and successfully shut off the flow-control valve.

There was no damage to the facility or delivery systems. Members of the reentry party suffered minor frost-bite of their feet when their shoes became frozen to the water-wetted rear deck of the truck. The "freezing" of the shoes was caused by the extremely cold slush in which the men were standing. Operating personnel took action to control promptly all possible sources of ignition in the surrounding area, including shutdown of part of the plant. Water hoses, which had been charged prior to the operation, were brought into play in an unsuccessful attempt to freeze the leaking connection. With the leak developing into an uncontrollable situation, the operating personnel were faced with the choice of two alternatives:

1) to permit the leak to continue which, based on the estimated leak rate and the liquid hydrogen volume remaining in the tank, would have sustained the condition for up to 12 hours; or
2) to execute a re-entry plan to close the tank shut-off valve at the rear of the truck. The latter course of action was chosen, and members of a re-entry party, wearing protective clothing, were successful in closing the shut-off valve and terminated the leak.

The reason for this accident was that a loose hose flange connection allowed leakage of cold fluid through the fluorocarbon lubricated bayonet seal. This leak allowed cold cryogenic fluid to contact and shrink the O ring seal, made of nitrile synthetic rubber, thus permitting liquid hydrogen leakage to the atmosphere.

Author's comment

The obvious comment could be that if the O ring was designed for low temperature service the leakage could not have happened. But then, O rings cannot be designed for operational faults such as this.

However, from this operating experience one can learn that, working in the midst of a cryogenic environment is a highly hazardous practice and use of a tanker-trailer which does not have a safely accessible auxiliary shut-off valve is unsafe in the event of a spill.

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16.5 Case Study

Pebble Mill

Pebble Mill where flint rock media (as opposed to normal steel balls) is used against which the mill's interior is protected by a 75 mm rubber lining over a metal sandwich of 6 mm stainless steel, welded to 60–100 mm carbon steel plate [6].

Oxiana, an Australian copper and gold mining and exploration company, developed the Sepon copper and gold mines in Laos over the past five years and now produces up to 60,000 t/y of copper cathodes and more than 200,000 oz/y of gold in that country. Sepon is the first major mining project in Laos and represents the beginning of a promising mining industry there. The project is now the largest private business in Laos and the biggest private employer. Oxiana is exploring for copper and gold deposits in other parts of Laos. Currently Sepon hosts eight separate gold deposits and the Khanong copper deposit. Each of five gold deposits comprises pits that are mined to extract the ore. Ore and waste are mined from the Khanong pit 24 hours per day, 365 days grinding.

Oxiana faced an interesting technological challenge in providing a copper mill which needed to operate in a very aggressive processing environment. The pulp in the mill contains large quantities of sulphuric acid with a pH level less than 1. The engineers could have put in multiple small vertical mills and scrubbers, but the number of machines required would have been uneconomic and produced a complicated plant. Engineering multiple machines into a circuit like this is not a preferred option. It will be best to keep it simple, for reliability and efficiency. The project was managed by engineering the design of a single stage high-efficiency pebble mill. It used flint rock media (as opposed to normal steel balls), against which the mill's interior is protected by a 75 mm rubber lining over a metal sandwich of 6 mm stainless steel, welded to 60–100 mm carbon steel plate. According to Oxiana mining companies are generally pioneering technologically.

16.6 Case Study

Rubber and Ceramic Liners

Longer life of Rubber-Ceramic liners-alternate material selection [7].

The Kidd Creek Division of Falconbridge, Ltd. has been mining copper, lead/zinc, and silver in northern Ontario since 1964. Kidd Creek mines 7,000 feet deep to supply the milling operation with 9,000 tons of product per day.

A critical part of the Kidd Creek mining, milling, and smelting operations is the partnering relationship between Kidd Creek and Durex plus Durex engineering, manufacturing, customer service, and outside material suppliers. All of these people are dedicated to achieving less downtime and greater productivity throughout the Kidd Creek Division.

For example, the very sharp, abrasive material mined by Kidd Creek is especially tough on screens, lining systems, and wear parts. On one circuit, a vendor's lining system, manufactured steel panels with ceramic flakes embedded in vulcanized rubber, kept washing out after a short wear life of less than 6 to 10 months. Kidd Creek personnel experimented with chrome white iron and chrome carbide overlay liners and raised the wear life to 11 months. When Durex was asked to evaluate the situation, Durex recommended a superior rubber/ceramic liner designed by embedding ceramic cylinders in a rubber matrix. This allowed an improved method of applying the strength of ceramic in the flexibility of rubber. Kidd Creek maintenance supervisors checked the data and agreed to give rubber/ceramic a try. The wear life of the new lining system is now 18 to 24 months. Rubber compounders develop their own proprietary formulations for specific application.

16.7 Case Study

Rubber Compound Development for FGD (Flue Gas Desulphurizing) Systems [8]

Highly corrosive and abrasive environments are encountered in FGD systems. Blair Rubber company developed suitable rubber composition for combating these severe duty conditions prevailing in the system. Blair Rubber company's performance linings for FGD components are based on chlorobutyl rubber with 60 Shore A durometer for the FGD absorber and associated demister internals. 60 Shore A durometer was specially designed for recycle slurry, reagent feed, gypsum dewatering, filtrate, piping, rake arms and agitators.

Numerous manufacturers in the early 70's experimented with pure gum rubber for absorber and component piping. The overwhelming evidence from these early installations showed that a soft 40 durometer natural rubber is unsuitable for these units and associated component piping. The linings failed rapidly due to blistering which was caused by moisture absorption.

Another critical factor in preventing blistering is the moisture permeation rate, which is the determinant of FGD rubber life. This permeation rate is directly proportional to the temperature gradient across the rubber lining, the so-called "coldwall" effect.

Simulated FGD tests conducted by EPRI [9] (Electric Power Research Institute CA USA, is an independent, non-profit company performing research, development and design in the electricity sector for the benefit of the public) showed that both fully cured and deliberately uncured pure gum 40 durometer natural rubbers do blister. Panels of the same lining, when externally insulated, did not blister during the test period. Also, tests confirm blistering did not occur with 60 durometer compounds either with or without insulation. Laboratory tests comparing various durometer materials showed vast differences in water absorption. A 40 durometer natural rubber gains five times the amount absorbed by a 60 durometer lining.

FGD Absorber case histories confirm that the chlorobutyl linings give trouble free service when correctly applied and cured. Chlorobutyl linings offer excellent chemical, heat, weather and ozone resistance compared to natural rubber.

However, the 60 durometer natural rubber specifically compounded for the FGD rubber absorption pipe has double the abrasion resistance compared to the chlorobutyl linings used in FGD absorbers. In selecting a rubber lining for pipe, either for recycled slurry, reagent feed, gypsum dewatering, or filtrate systems, one must take into account the volume flow, percentage of solids and particle size in order to make the proper choice. Where abrasion is considered severe, a 60 durometer natural rubber is the proper selection. When moderate to light abrasion is encountered, 60 durometer chlorobutyl lining may be the choice.

In many FGD pipe applications, 40 durometer pure gum rubber gives only 3–7 years of service where a 60 durometer natural rubber gives 7–10 years of life. Since most FGD scrubber piping is very light abrasion, installing chlorobutyl is expected to last in excess of 15 years. Chlorobutyl is recommended as the performance lining for the absorber and the demister supporters.

16.8 Case Study

Wrong Selection of Curing Method

Grasim Industries is a part of the $29.2 billion corporation and premium conglomerate, the Aditya Birla Group, a dominant player in almost all chemical industry sector, and one of the Fortune 500 business enterprises. The Caustic Soda and Chlorine manufacturing division is situated in Nagda, Mathya Pradesh, India.

Back in the year 1981, the author was engaged in the development of a suitable ebonite compound for the hydrochloric acid storage tank lining and its vulcanization methods at Grasim's site at Nagda for the contracting company MIL Industries Ltd., Chennai, India. The transportation of the tank of size 2-m dia and 6-m long to the rubber lining vendor's factory was not found to be an economical proposition at that time because of the cost and distance involved and as per request of the Grasim's engineers who were under project constraints, the rubber lining and curing at their site was resorted to by compulsion.

A suitable ebonite compound of 80 shore D curable at a low temperature was developed and the curing was advised to be carried out at an atmospheric pressure of 1 bar (one bar atmospheric pressure is 14.696 psi which is also equivalent to 1 atm pressure) with steam, the tank being properly insulated from outside to contain the heat within, for a curing period of 48 hrs. The tank was a closed one with one end having a dished end welded to the shell and the other having a bolted dish. The tank was designed as a storage tank with a wall thickness of 5 mm to withstand the hydrostatic pressure of the fluid it holds. The tank was rubber lined with the 80 shore D compound and all manholes and nozzles were closed and an extra pipe length of 1 meter was welded to one of the nozzles to maintain water level inside the tank. The tank was filled with water and steam was introduced through a header pipe and air at atmospheric pressure pumped into the water for effecting agitation for homogeneous distribution of heat. The temperature of steam at 1 bar was measured with thermometers fixed on the pockets welded to the tank, which later was meant to be supports for the tank. The curing was undertaken on a cold weather day in upper northern India and the temperature shown in the thermometer was lower than 90°C. With an intention of increasing the temperature to 100°C, the operator ignorantly increased the steam pressure to 3 kg per sq cm which exceeded the withstanding capacity of the tank and it bursted off, exploded and the welded dished end detached itself from the main body of the tank and flew to a distance of about 500 feet. Since it was a nighttime shift having less movement of operators, no casualty occurred in what otherwise could have been a fatal accident.

Investigations by the client and vendor companies were ordered and the obvious reason was found to be high pressure beyond the pressure rating of the tank even though it was hydraulically tested for 1.5 times the working pressure which was only up to 1.5 kg per sq cm against the pressure during the accident being

3 kg per sq cm. The important lesson to be learned from this episode is that no vessel should be used as an autoclave unless it is designed for that pressure for the purpose of curing.

A few cases of rubber lining applications are given below:

16.8.1 Feed Launders for M/s. Hindustan Dorr-Oliver Ltd, India

Iron ore with a solid content of 25%–30% in water was being handled in these feed launders. The velocity of the slurry was 2 ft per second. A 6 mm thick soft natural rubber compound of hardness 40°A was found to be well suited for this application.

Acid handling Bins for M/s.Ceylon Mineral Sands Corporation, Sri Lanka.

The materials handled in the bins were 20% solids by weight, flow of 2.9 tons of water per hour and 47 gallons/minute of pulp. The size of the material was 100 to plus 325 BSS mesh. Maximum acid concentration was 20% hydrochloric acid. The temperature in the system was 60°C. A 6 mm thick natural rubber lining of shore hardness 50°A was used to protect the equipment against the abrasive environment as well as the corrosion effects of hydrochloric acid.

16.8.2 Regrinding Ball Mill in the Copper Project at Khetri in Rajasthan, India

For wet grinding of copper ore in the ball mills at ambient temperature a 6 mm thick natural rubber compound of 45°–50°A was used successfully as an abrasion resistant layer.

16.8.3 Pipes, Launders and Chutes in an Iron Ore Mining Project in Karnataka, India installed by M/s. Canadian Metchem, Canada

Pipes of different diameters of 25 mm up to 450 mm and length running over a total of 12 kilometers and in lengths of 1 m to 6 m and launders and chutes were protected with abrasion resistant soft natural rubber lining of hardness 40°A of thickness varying from 6 mm to 10 mm using a chemical adhesive bonding system serving well for over ten years. The rubber lined pipes used victaulic couplings with grooves fixed with natural rubber sealing rings for joining since the pipes were flangeless. The pipes are transporting iron ore slurries of specific gravity 1.02 to 2.3 with a slurry velocity of 6m/s.

16.8.4 Rotary Vacuum Drum Filters Designed By M/s. Eimco, USA

These filters were used in illmenite beneficiation and titanium dioxide plants. These and their parts like agitators, troughs etc., were lined with a semi-hard flexible ebonite of natural rubber to protect the equipment against the abrasive action of the ore and solid particles in the slurries.

16.8.5 Spherical Digesters in a Chlor-alkali Plant India

Illmenite sand with steam and hydrochloric acid was handled in the spherical digesters. The temperature in the digesting process was ambient to more than 130°C. Therefore brick lining was applied on a butyl rubber lining 5 mm thick with hardness of 55°A. The rubber serves as a cushioning medium beneath the brick lining, as well as resisting the temperature at the brick rubber interface of about 100°C.

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Glossary of Terms

This glossary explains terms related to the manufacture, preparation, application and testing of rubber linings and allied materials used in the protective linings industry.

Abrasion resistance – The resistance of a material to loss of surface particles due to frictional forces.

Acid resistance – The ability to resist the action of acids within specified limits of concentration and temperature.

Activator – A chemical used in rubber compounding in small quantities to increase the effectiveness of an accelerator.

Adhesion – The force in which two surfaces are held together. Adhesion values for tank lining are often determined by the procedures described in ASTM D429-Test Methods for Rubber Property-Adhesion to Rigid Substrates.

Age resistance – The resistance to deterioration by oxygen, heat, light, ozone, alone or in combination, during storage or use.

Age resistor – Also known as an antioxidant, a chemical that when added to a rubber compound will retard deterioration due to heat, light, oxygen, alone or in combination thereof.

Ambient temperature – The temperature of the atmosphere or medium surrounding the object under consideration.

Antioxidant – Same as age resistor, a chemical compounding material used to retard deterioration caused by oxygen.

Antiozonant – A chemical compounding material used specifically to retard deterioration caused by ozone.

ASTM – American Society for Testing and Materials.

Atmospheric cracking – Small fissures in the surface of rubber articles resulting from exposure to atmospheric conditions.

Atmospheric steam cure – Same as exhaust steam cure.

Autoclave – A pressure vessel used for the curing or vulcanization of rubber parts by means of steam under pressure.

Blasting – Surface cleaning and preparation of substrate using abrasives such as airborne sand, grit or shot.

Blast profile – A measure of surface roughness.

Blemish – A superficial mark or impression on the surface of green or cured rubber lining.

Blister – A cavity deforming the surface of a material usually due to expansion of an entrapped liquid or gas. Permeation failures of tank linings in service is sometimes evidenced by blister formation.

Bloom – A discoloration or change in appearance of the surface of a rubber product caused by the migration of a liquid or solid to the surface. (Examples: sulfur bloom, wax bloom.) Not to be confused with dust on a surface from external sources.

Blow down – Periodic opening of the bottom drain in an autoclave or vessel during cure to remove condensate.

Bond – The union of materials by use of adhesives, usually used in relation to parts vulcanized after attaching or being assembled together.

Bonding agent – An adhesive used to bond rubber to metal or fabric.

Brick lining – One or more courses of brick laid on a cured tank lining. Used in high temperature applications for the protection of rubber linings.

Buffing – The grinding of a surface producing a roughened surface. Usually done to obtain dimensional conformance, or as a preparation for repair.

Butt seam – A seam made by placing two pieces to be joined edge to edge.

Butt splice – A joint made in a rubber part before or after vulcanization by placing the two pieces to be joined edge to edge.

Butyl rubber – A copolymer of isobutylene and isoprene rubber; ASTM designation IIR; butyl rubber is the common name for such materials.

Calender – A machine equipped with two or more heavy, internally heated or cooled rolls, used for the continuous sheeting or plying up of rubber compounds.

Calender blister -Trapped air between calender plies of a multiply rubber buildup.

Cement – A dispersion or solution of an elastomer or compound in a solvent for use as an adhesive or coating.

Chalking – The formation of a powdery residue on the surface of a material resulting from degradation.

Checking – Short, shallow cracks on the surface of a rubber product, resulting from environmental conditions.

Chemical cure – A tank lining system which can cure at low temperatures by topically applying a liquid curing agent.

Cholorbutyl – Used in a general sense to mean a chlorobutyl tank lining construction. ASTM designation CIIR.

Chlorosulfonated polyethylene – Generic name of an elastomeric material sold as Hypalon ASTM designation CSM.

Coefficient of thermal expansion – The fractional change in dimension of a material for a unit change in temperature.

Coefficient of friction – Between rubber and dry surfaces, the ratio of the force required to move one surface over the other to the force pressing the two surfaces together.

Cohesion – The attraction between molecules of a substance, and the property which prevents separation of a substance into parts when acted upon by external forces.

Cold bond cement – A cement used to repair the lining to be cured at ambient temperature.

Compatibility – The ability of different materials to blend and form a homogeneous system. Also, the ability of different tank lining materials to adhere and function together.

Composite – A homogeneous lining created by the assembly of two or more rubber stocks with other materials like fabrics.

Compound – An intimate mixture of rubbers with all the ingredients necessary for the finished article. Sometimes called stock.

Condense – Water from condensed steam which lies in the bottom of a pressure vessel or exhaust steam cured tank. It can prevent proper cure.

CR – ASTM Designation for Chloroprene rubber (neoprene).

Cracking – A sharp break or fissure in the surface of rubber articles that develops on exposure to light, heat, ozone or repeated bending or stretching. Harsh chemical exposure can lead to gradual cracking of linings.

Crazing – A surface effect on rubber articles characterized by many minute cracks. This is generally not a serious degradation for a tank lining, unlike cracking.

Creep – The deformation in either vulcanized or un-vulcanized rubber under stress that occurs in time after the immediate deformation.

Cross linking – When chemical bonds set up between molecular chains, the material is said to be cross linked. Once cross linked, materials cannot be reprocessed. A form of curing.

Crystallinity – Orientation of disordered long chain molecules of a polymer into repeating patterns. Degree of crystallinity affects stiffness, hardness, low temperature flexibility and heat resistance. Crystallinity can make some linings still and boardy, difficult to lay.

CSM – ASTM designation for chlorosulfonated polyethylene (Hypalon).

Cure – Similar to cross linking, while cure covers all types (sulfur, peroxide, radiation, etc.).

Cure time – The time required to produce vulcanization at a given temperature. (Cure time varies widely, being dependent on the type of compounding used and the thickness of the product.)

Curing agent – A chemical which will cause cross linking to occur.

Damping – The ability of a material to absorb energy to reduce vibration.

Deformation – A change in the shape or dimensions of a body, resulting from stress, strain.

Delamination – Separation or splitting, either between plies in laminated goods or occasionally within the homogeneous part itself.

Density – The mass (weight) per unit volume of material (lbs/cubic foot or grams/cubic centimeter).

Dew point – 1) The temperature of the air at which dew begins to be deposited. 2) The temperature at which a given sample of air will have a relative humidity of 100%.

Dielectric strength – The measure of a product's ability to resist passage of a disruptive discharge produced by an electric stress.

Double bond – A double union of two carbon atoms instead of one union. Materials containing double bonds are chemically unsaturated.

Drain – The line leading from the bottom of an autoclave.

Durometer – An instrument for measuring the hardness of rubber. The "A" durometer scale is used for flexible materials and the "D" for rigids.

Durometer hardness – A value that indicates the indentation or resistance to indentation of the indentor point of a durometer. High values indicate harder materials. See ASTM D2280-Test Method for Rubber Property-durometer Hardness.

EPDM – ASTM abbreviation for a terpolymer of ethylene, propylene, and a diene with the residual unsaturated portion of the diene in the side chain.

Ebonite – A term for natural hard rubber.

Elastomer – A polymeric material which, at room temperature, is capable of recovering substantially in shape and size after removal of a deforming force.

Elongation – Extension produced by tensile stress, usually expressed as a percent of original unit length.

Embrittlement – A rubber compound becoming brittle during a low or high temperature exposure or as a result of ageing.

Exhaust steam cure – Non-pressurized steam cure. A method commonly used for large tanks which cannot be pressurized.

Exothermic – A chemical reaction in which heat energy is liberated. In tank linings, very thick layers of ebonite compounds may exotherm during cure.

Extraction – The process of removing one or more components of a homogeneous mixture by treating the mixture with a liquid (solvent) in which the components to be removed are soluble but not the mixture as a whole.

Fish eye – A thin elongated void in a calendered sheet. A surface imperfection. Not detrimental to service life.

Flow marks –imperfections, cracks in the surface, causes flowing in uncured rubber.

Freshening – solvent washing of a rubber surface to provide tack.

Gasket – A deformable material clamped between essentially stationary faces to prevent the escape of matter through an opening or joint.

Gauge (gage) – Refers to a dimension, of the thickness of a rubber lining.

Grain – The unidirectional orientation of rubber or filler particles occurring during processing (extrusion, milling, calendering) resulting in anisotropy of a rubber vulcanizate.

Green strength – 1) The resistance to deformation of a rubber stock in the uncured state. 2) Uncured adhesion between plied or spliced surfaces.

Halogen – Class of elements containing chlorine, bromine, iodine, and fluorine.

Hardness – The measured resistance to indentation of a material. See durometer.

Hard rubber – Ebonite.

Heat aging – A procedure where vulcanized rubber is ageing in air or oxygen at elevated temperatures.

Heat resistance – The property or ability of rubber articles to resist the deteriorating effects of elevated temperatures.

Holiday – A small uncovered or non-coated area in a substrate; usually refers to pinholes in thin coatings of rubber sheeting.

Hydrocarbon – An organic chemical compound containing the elements carbon and hydrogen. Aliphatic hydrocarbons are straight chain compounds and aromatic hydrocarbons are based on the cyclic or benzene ring. They may be gaseous, (methane, ethylene, butadiene); liquid (hexane, benzene); or solid (natural rubber, naphthalene, cis-polybutadiene).

Hot water cure – A method for curing rubber in hot or boiling water. Colloquial.

Hydrolysis – Chemical decomposition of a substance involving a reaction with water.

Hysteresis – The heat generated by rapid deformation of a vulcanized rubber part. It is the difference between the energy of the deforming stress and the energy of the recovery cycle.

IIR – ASTM designation for isoprene rubber, cis- or trans-polyisoprene are examples.

Immersion testing – Commonly used to determine the resistance of tank lining compounds to various chemicals. See ASTM D-471-Test Method for Rubber Property-Effect of Liquids.

Impression – A design formed on the surface of a rubber article by a method of transfer, such as fabric mold, embossed poly impression.

Inhibitor – A chemical that is added to a system to slow down or prevent the rate of corrosion, as in a monomer to prevent its premature polymerization.

Inorganic chemical – Chemicals whose composition is based on atoms other than carbon (salt, clay, silica, caustic, hydrochloric acid, etc.).

Intermediate primer or cement – A primer or cement which is part of a total tank lining adhesive system.

Internal steam pressure cure – A rubber-lined vessel which can be sealed and is structurally strong enough to take steam pressure during cure. Examples are railroad tank cars and chemical reactors.

Liner – A separator, usually of cloth, used to prevent adjacent layers of material from sticking together.

Mechanical properties – Physical properties of a material associated with reaction to various applied forces, as in tensile strength, compression set, elongation, DeMattia Flex, etc.

MEK – Methylethyl ketone. Solvent used in some cements and primers.

MIBK – Methylisobutyl ketone. Solvent used in some cements and primers.

Micrometer – An instrument by which highly accurate minute measurements of length, depth, or thickness may be made.

Migration – The movement of materials within a rubber product to its surface, or from an area of high concentration to one of low concentration, or into another material to which it is laminated.

Migration stain – A discoloration of a surface by a rubber article which is adjacent to but not touching the discolored surface.

Modulus – In the testing of rubber, it is the force in per unit area lbs/in^2 or mega-pascals of initial cross-sectional area necessary to produce a given percentage of elongation.

Modulus of elasticity – Ratio of stress to strain within the elastic range. Same as Young's modulus.

Mpa – The abbreviation for mega-pascal, a metric unit of measurement.

Natural rubber – Rubber formed in a living plant or tree, usually referring to Hevea Brasiliensis. ASTM designation NR.

NBR – ASTM designation for copolymers of acrylonitrile and butadiene.

Neoprene – Originally the trade name, now the generic name of polymers and copolymers based on chloroprene. ASTM designation CR.

Nerve – The elastic resistance of raw rubber or compounds to permanent deformation during processing. A nervy tank lining will be difficult to lay around tight bends or in corners because of springback.

Nitrile rubber – Copolymers of acrylonitrile and butadiene. Same as NBR or Buna-N.

Non-staining – An accelerator, antioxidant or similar substance that will not discolor other goods placed next to the rubber in which it is used. Sometimes used as well to describe non-discoloring in white or colored goods.

NR – ASTM designation for natural rubber.

Oil resistance – The ability to withstand swelling and deterioration by a specified oily liquid. None of the available elastomers are oil proof. Some elastomers are oil resistant to varying degrees.

Oil swell – The change in volume of a rubber article resulting from contact with oil.

Open steam cure – A method of vulcanization in which the steam is in direct contact with the product being vulcanized at atmospheric pressure.

Optimum cure – The time and temperature of cure necessary to develop the desired combination of properties.

Organic – Refers to chemical structure based on the carbon atom, natural and synthetic.

Overcure – A state of vulcanization beyond the optimum, often resulting in a decline in certain physical properties. Usually indicated by a sticky or gooey rubber surface.

Oxidation – The reaction of oxygen with a rubber product, usually accompanied by a change in feel, appearance of surface, or a change, usually adverse, in physical properties.

Ozone (O_3) – An allotropic form of oxygen. A gas with a characteristic odor which is a powerful oxidizing agent. It is present in the atmosphere at low levels and causes cracking in certain types of elastomeric compounds when they are stretched or compressed.

Ozone cracking – The surface cracks, checks or crazing caused by exposure to an atmosphere containing ozone.

Ozone resistant – Having the ability to withstand the deteriorating effects of ozone (generally cracking).

Permanent set – The percentage by which an elastic material fails to return to its original form after deformation.

pH – The measure, on a logarithmic scale of 1 to 14, of the relative acidity or alkalinity of an aqueous solution. Neutral pH (pure water) is 7. Hydrochloric acid would be approximately 1 and sodium hydroxide approximately 13.

Phase – A physically homogeneous, mechanically separable portion of a material system.

Plastic flow – The deformation of a plastic material beyond the point of recovery, accompanied by continuing deformation with no further increase in stress.

Plasticity – The tendency of a material to remain deformed after reduction of the deforming stress to or below its yield stress.

Plasticizer – A substance incorporated into a material to increase its workability, flexibility or distensibility.

Ply adhesion – The force required to separate two adjoining plies in a specified width of a rubber product.

Ply separation – A condition which occurs due to a loss of adhesion between plies.

Polymer – A macromolecular material formed by the chemical combination of monomers having either the same or different chemical composition.

Polymer chain – The chain of elements that form the basis of the structure of a polymer. The elements may be all carbon atoms, carbon and oxygen, silicone, nitrogen, etc.

Precure – Premature vulcanization taking place during the process prior to vulcanization. Similar to scorch.

Pressure cure – Vulcanization under pressure.

Profile – Surface profile is a measure of the roughness of a surface which results from abrasive blast cleaning. The height of the profile produced on the surface is measured from the bottom of the lowest valley to the top of the highest peak.

Primer – A coating applied to the surface of a material, prior to the application of an adhesive; sometimes considered as a part of the adhesive system.

PSI – The abbreviation for pound per square inch.

Rate of cure – The relative time required to reach a predetermined state of vulcanization under specified conditions.

Recovery – The degree to which a rubber product returns to its normal dimensions after being distorted.

Reinforcement – The stiffening effect of solids, such as carbon black, on an unvulcanized elastomer mixture and the enhancement of the physical properties of the vulcanized compound, such as tensile, elongation, modulus, abrasion resistance, tear, etc.

Resilience – The ratio of energy output to energy input in a rapid (or instantaneous) full recovery of a deformed specimen.

Reversion – The softening of vulcanized rubber when it is heated too long or exposed to elevated temperatures. It is a deterioration in physical properties. (extreme reversion may result in tackiness.) This most commonly affects natural rubber linings.

Rubber – An elastomer, generally implying natural rubber, but used loosely to mean any elastomer, vulcanized and unvulcanized. By definition, a material that is capable of recovering from large deformations quickly and forcibly.

Saddle – The rubber lining applied to the outside center area of tank cars for protection from acid spills when loading or unloading.

Sags – Sag marks – voids created by the flow of uncured rubber.

Sand blast – To clean with sand or steel grit in a high velocity stream of air.

Scorch – Premature vulcanization of a rubber compound, generally due to excessive heat history.

Seam – A line formed by joining material to form a single ply or layer. A splice or overlap.

Security strip – A strip of material laid over a joint.

Semi-cure – A preliminary incomplete cure applied to an article in the process of manufacture, to cause the rubber to acquire a degree of stiffness or to maintain some desired shape.

Service test – A test in which the product is evaluated under actual service conditions.

Set – Percentage of deformation remaining after complete release of the force producing the deformation.

Shelf aging – The natural deterioration of rubber articles kept in storage or on the shelf under normal atmospheric conditions. This slow deterioration is due primarily to oxygen and ozone attack.

Shelf life – An expression describing the time a material can be stored without losing any of its properties.

Shore hardness – A term denoting a hardness value derived from an instrument developed by the Shore Instrument & Mfg. Co., Inc.

Skive – A cut made on an angle to the surface to produce a tapered or feathered edge.

Skive butt seam – Two skived edges joined edge-to-edge to form a smooth surface. Usually each edge is cut at a 45° bevel so the seam fits snugly.

Soapstone – A soft powder or stone, basically hydrated magnesium silicate, having a soapy feel, used to dust the surface of un-vulcanized rubber compounds to keep them from sticking together. Similar to talc.

Soft rubber – A term used for rubber which cures under 70 durometer "A" scale.

Spark tester – A high voltage test unit used to detect breaks or pinholes in a lining.

Specific gravity – The ratio of the mass of a unit volume of a material to that of the same volume of water at a specified temperature.

Spot cure – A localized area being cured. Commonly used with repairs.

State of cure – The cure condition of a vulcanization relative to that at which optimum physical properties are obtained.

Steam cure (open) – A method of vulcanizing rubber parts by exposing them directly to steam.

Stiffener – A steel beam on the outside of a tank being lined. They often act as a heat sink and will have an influence on cure state.

Stitching – A method of joining two pieces of uncured rubber compound together by means of a stitching roller, and a hand held tool comprised of a wheel with a narrow edge which is often serrated. It is commonly used to make tank lining joints.

Stock – An uncured rubber compound of a definite composition from which a given article is manufactured.

Strain – Deformation resulting from a stress.

Stress – Force per unit of original cross sectional area that is applied to a part or specimen.

Stress relaxation – The time dependent decrease in stress for a specimen at constant strain.

Substrate – The surface on which a coating or lining is applied.

Sun checking – Surface deterioration in the form of cracks, checks or crazing caused by exposure to direct or indirect sunlight.

Surface preparation – The preparation of a substrate prior to applying tank lining: welding, grinding, blasting, cleaning.

Surge – To rise suddenly to an excessive or abnormal value.

Surge pressure – The maximum pressure reached at surge, frequently the result of rapidly activating a valve.

Swelling – An increase in volume or linear dimension of a specimen immersed in liquid or exposed to a vapor.

Tack – The property of a polymer, compound, or adhesive that causes two layers to stick together on application of mild pressure. Tacky polymers or compounds do not necessarily stick to other surfaces.

Tack cement – A formulated rubber/cement mixture which can be rolled or brushed on surfaces which will hold the rubber panel in place until cure takes place. Normally considered a part of the adhesive system.

Tensile strength – The maximum tensile stress applied during stretching of a specimen to rupture expressed per unit area of the specimen, i.e., PSI and Mpa.

Tensile stress – The applied force per unit of original cross-section area of a specimen.

Thermosetting – Capable of being changed into a substantially infusible or insoluble product when cured under application of heat or chemical means. Vulcanization is a type of thermosetting.

Tie gum – An intermediate layer of rubber employed to promote bonding of two surfaces; usually a soft rubber compound.

Tight cure – A cured state where high degree of cross linking has taken place. The best service life is obtained with a tight cure.

Tolerance – The amount by which a property of a material or object can vary from a specified value and still be acceptable.

Toluene – An organic solvent used in tank lining cements and primers.

Trapped air – Air that is enclosed between two materials; between steel and lining or two lining sheets. Note: trapped air can occur between vulcanized and un-vulcanized rubber.

Ultraviolet light – A form of energy occupying a position in the spectrum of sunlight beyond the violet, and having wavelengths of less than four micrometers which is the limit of visible light. UV (ultraviolet) rays are very active chemically, exhibit bactericidal action, and cause many substances to fluoresce. UV rays accelerate deterioration of rubber parts exposed to them and can initiate polymerization.

Under cure – A low state of cross linking. Often an under cured lining will be low in durometer hardness and fluid and acid resistance will be poor.

Vapor phase – Vapor above the liquid in a tank car or closed storage tank; often the most severe conditions for rubber tank lining.

Viscosity – The resistance of a material to flow either by gravity or under stress.

Vulcanizate – Preferably used to denote the product of vulcanization, without reference to shape or form.

Vulcanization – 1) An irreversible process during which a rubber compound, through a change in its chemical structure (cross linking), becomes less plastic and more elastic. Elastic properties are conserved, improved, or extended over a greater range of temperature. 2) It often refers to the reaction of rubber specifically with sulfur, while curing covers other methods of cross linking. Both terms are often used interchangeably.

Vulcanizing agent – Any material that can produce in rubber the change in physical properties known as vulcanization, such as Chemcure applied to chemical cure rubber linings.

Weathering – A surface deterioration of a rubber article during outdoor exposure.

Wetting agent – A substance that reduces the surface tension of a liquid, thereby causing it to spread more readily on a solid surface.

Wrapped cure – A vulcanizing process using a tensioned wrapper (usually fabric tape) to apply external pressure.

White metal blast – To sand or shot blast a steel substrate to a SSPC No. 5 finish, as specified by the Steel Structures Painting Council.

Xylene – An organic solvent used in tank lining cements and primers.

Yield point – The stress in a material, at which there occurs a marked increase in strain without an increase in stress. Rubber is said to have a zero yield point except under very rapid elongation and release.

Yield strength – The stress at which a material exhibits a specified limiting permanent set. Determined by a measurable value of plastic yielding of the material above which the material is considered to be damaged and below which the damaging effects are considered to be negligible.

Young's modulus – Stress per unit strain for perfectly elastic materials. The method of determination of Young's modulus in flexure of natural and synthetic elastomers at normal and subnormal temperatures is given in ASTM Method D 797.

Appendix 1

ASTM Elastomer / Rubber Designation

Abreviation	**Elastomer**
ABR	Acrylate Butadine
BR	Butadiene
CR	Chloroprene
EPM	Ethylene-propylene
EPDM	Ethylene-propylene diene
IR	Isoprene
IIR	Isobutylene, isoprene or butyl rubber
SBR	Styrene butadiene
SIR	Styrene-isoprene
NBR	Acrylonitrile-butadiene
NCR	Acrylonitrile-chloroprene
PBR	Vinyl pyridine-butadiene
PSBR	Vinyl pyridine styrene butadiene
XNBR	Carboxylic-acrylonitirle-butadiene
CIIR	Chloroisobutylane-isoprene or chlorobutyl rubber
BIIR	Bromoisobutylene-isoprene or bromobutyl rubber
MQ	Dialky siloxane
GPO	Poly (Propylene oxide)

Abreviation	**Elastomer**
AU	Polyesterurethanes
EU	Polyetherurethanes
CSM	Chlorosulphanated polyethylene
T	Thiokol
FKM	Fluorinated rubbers-Vitons
FC, FE, GE	Silicone rubbers
FK	Fluorosilicone rubbers

Appendix 2

Properties of Specialty Elastomers

Specialty materials offer properties or combinations of properties not available in any other class of materials. With extreme high temperature and low temperature resistance, extreme chemical resistance and stability over a wide range of operating conditions, these materials perform where no others can.

Trade name	**Silicone**	**Flourosilicone**	**Thiokol**	**Viton**
Max. Tensile (psi)	1700	1500	1200	2000
Max. Elongation %	700	300	300	300
Compression set resistance	Very good	Good	Poor	Good
Resilience	Good	Excellent	Fair	Fair
Tear/Chip resistance	Poor	Poor	Poor	Good

Trade name	**Silicone**	**Flourosilicone**	**Thiokol**	**Viton**
Abrasion resistance	Fair to Poor	Poor	Poor	Good
Service temp. (°F)	−150 to 600	-80 to 300	−65 to 160	−10 to 600
Atmospheric aging	Excellent	Excellent	Good	Excellent
Ozone resistance	Excellent	Excellent	Excellent	Excellent
Oxidation resistance	Excellent	Excellent	Good	Excellent
Solvent resistance	Poor	Poor	Good	Poor
Acid resistance dilute	Very Good	Very Good	Good	Excellent
Acid resistance concentrated	Fair	Fair	Fair	Good
Gasoline/Oil resistance	Poor	Excellent	Excellent	Excellent
Animal/ Veg. oil resistance	Fair	Excellent	Poor	Excellent
Adhesion to metals	Very good	Good	Poor	Good
Adhesion to fabrics	Very good	Good	Fair	Good
Noteworthy properties	Heat resistance excellent; release characteristics non stick	Does not have the resistance of silicone	Superior oil resistance	Heat, oil & solvent resistance

Appendix 3

Temperature-pressure Equivalents of Saturated Steam

Various curing conditions are followed for various product lines. The following are temperature-steam pressure equivalents of saturated steam at sea level. Source: Steam Tables of Marks and Davis, Longmans Green & Co.

1 Atmosphere = 101.325 kPa = 14.696 psi = 1.0335 kgs/sq cm^2

Psi	Kgs/sq cm^2	kPa	Temperature	
			°C	°F
0	0.000	0.0	100.0	212.0
10	0.730	68.9	115.2	239.4
20	1.406	137.9	126.0	258.8
30	2.109	206.8	134.5	274.1
40	2.812	275.8	141.5	286.7
50	3.515	344.7	147.5	297.7
60	4.218	413.7	153.0	307.4
70	4.921	482.6	157.8	316.0

Psi	**Kgs/sq cm^2**	**kPa**	**Temperature**	
			°C	**°F**
80	5.625	551.6	162.1	323.8
90	6.328	620.5	166.2	331.2
100	7.031	689.5	169.9	337.8
110	7.734	758.4	173.4	344.1
120	8.437	827.4	176.7	350.1
130	9.14	896.3	179.8	355.6
140	9.843	965.3	182.7	360.9
150	10.546	1034.2	185.5	365.9
160	11.249	1103.2	188.1	370.6
170	11.952	1172.1	190.7	375.3
190	13.358	1310.0	195.4	383.7
200	14.061	1379.0	197.7	387.9
210	14.760	1448.0	199.8	391.6
220	15.470	1517.0	201.7	395.4

Appendix 4

List of Suppliers Who Publish Technical Literature on Rubber and Chemicals

The literature on rubber technology is largely scattered through numerous books on specialized topics, periodicals, conference proceedings and papers, trade literatures and brochures and catalogues, national and international standard specifications, patent literatures and government documents. The knowledge sector in rubber is continuously increasing as newer raw materials enter the scenario and newer production technologies develop and the old technologies continue to prevail as they have not yet proved to be obsolete and the newer technologies are craving for new applications racing with the all round development of science and technology. It is a complex task for the rubber technologist to keep track of many developments in the scientific fields, all of which always demand rubber or its allied high polymeric products. If one is not very much skilled in the art of science, technology or engineering, all rubber literatures will seem ambiguous and vague. A working knowledge of what rubber does is necessary to understand the technology.

Valuable literature on practical aspects in rubber technology is available in raw material suppliers' brochures and a few of their names and addresses are appended below. They are only sources of information to the technically trained people but not necessarily intended for workers in research and development.

1. American Cyanamid Co; Rubber chemicals Dept, NJ, USA. *Rubber chem. Lines, Caynamid Rubber Chemicals, and individual booklets on acrylic elastomers, methane elastomers etc.*
2. Ashland Chemical Co; P O Box 1503, Houston, Texas USA, *Carbon Black Board, TechNews.*
3. Cabot Corporation, Boston Massachusets, USA, *Cabot Technical Reports.*
4. Cities Services Company, Columbian Division, Akron, Ohio, USA, *Colombian Colloidal Carbons.*
5. Copolymer Rubber and Chemical Corp. Baton Rouge, La, *Epsyn Technical Data, NYsyn Technical data, SBR technical Bulletin.*
6. Malaysian Rubber Research and Development Board, *Malaysia Rubber Developments* and other technical literatures.
7. Goodyear Tire and Rubber Co; Akron, Ohio, USA, *Tech Book Facts.*
8. International Synthetic Rubber Co; Ltd; Hampshire, England, *Technical Information Sheets.*
9. Midland Silicones Limited; Emerson, NJ USA, *Technical Data Sheets-Silicones.*
10. Monsanto Co; Springside Drive, Akron, Ohio, *Technical Bulletins.*
11. Natural Rubber Bureau-Natural Rubber Producers' Research Association and the Rubber research Institute of Malaysia, Malaysia and Washington DC, *Natural Rubber and Technical Information Sheets.*
12. Enjay Chemical Co; Elastomers Department, Houston, Texas USA, *Enjay Polymer Laboratories' Technical Information Sheets, Formal Reports-Compounding.*
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About the Author

V. C. Chandrasekaran earned his BS Chemistry at the American College, Madras University, India in the 1950s and did his Licentiateship at the Institution of Rubber Industry (LIRI) in London in the 1960s. He was one of a few IRI gold medallists in India. He has served the rubber industry since 1960 starting his career with M/S TVS Ltd; a well known auto ancillary manufacturer in India as Production Superintendent. He then served M/S. Deccan Enterprises P. Ltd, M/S. Fenner India Ltd; and M/S. MIL Industries Ltd; India who are pioneers in fabrication and construction of chemical plant and equipment and anticorrosive rubber lining of process equipment as Rubber Technologist and Chief of Research and Development Division. Later, in the Indian Air Force, he served as a Senior Scientific Officer developing airborne rubber components for the aircraft, helicopters, and air weaponry of British, Russian and Indian origin.

Mr. Chandrasekaran has travelled widely in the Middle East and is a frequent traveller to the US. He participated in the rubber international event in Kuala Lumpur Malaysia in the 1980s representing one among a group of technical delegates from India. He has been on the faculty for various technical seminars conducted by the Fertilizer Association of India, National Productivity Council, Institute of Mechanical and Chemical Engineers, Institute of Plant Engineers and other Government and private sector sponsored forums on various areas of rubber technology and its applications. He promoted a few rubber projects as project consultant. He served as Managing Director in M/s Lebracs Rubber Lining P Ltd; Pondicherry, India and M/s. O R Elastomers P Ltd; Chennai, India.

The author had written three books namely *Essential Rubber Formulary; Tank Lining for Chemical Process Industries; Rubber Seals for Fluid and Hydraulic Systems* for the respective leading publishers: William Andrew Inc; New York, iSmithers RAPRA U K, and Elsevier. Currently, he is serving Can C Consulting India as a Consultant Rubber Technologist.

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